ANNUAL PROGRAM REVIEW

CORROSION CONTROL

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RECOVERY BOILER CORROSION

PROJECT F018

ANNUAL RESEARCH REVIEW

March 26, 1997

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TECHNICAL PROGRAM REVIEW

Project Title:	RECOVERY BOILER CORROSION
Project Number:	F018
Division:	Chemical and Biological Sciences
Project Staff:	P. Singh, G. Fonder, S. Al-Hassan
FY 96-97 Budget:	$45,000

Program Objectives:
Improve safety and increase operating life of equipment by proper selection of construction materials, suitable process conditions, and by understanding the possible corrosion processes in kraft recovery boilers.

Project Summary:
This section describes projects, which are directly funded by member dues, as well as other projects at IPST, related to corrosion in kraft recovery boilers.

High temperature sulfidation tests on SA-210 carbon steel in 1% H_2S gas were conducted at temperatures ranging from 320°C to 480°C. A series of 22 tests were done where the test times ranged between 4 to 72 hours. These tests were done to understand the basic kinetic changes in the corrosion process during the first few days of exposure of the boiler tube material. There are two main objectives for doing these tests:

a) to develop a better understanding of kinetic changes occurring during the initial stages of corrosion in this material/environment system;
b) to establish an experimental baseline for the tests to study the effects of the presence of smelt on the corrosion characteristics of SA-210 in 1% H_2S environments.

These objectives are directly related to the development of the corrosion kinetics database under the DOE/AF&PA project. Relevant data from various published sources are being collected and entered into this database. Test times for the published results range from less than an hour to thousands of hours. Mostly corrosion rates are averaged over the test time unless the weight changes are monitored continuously. Data generated at IPST and PPRIC in the past are of direct relevance to kraft recovery boiler conditions; however, most of the previous tests were done for relatively longer time periods (>100 hrs). The present set of tests has given us an understanding of initial changes in the reaction kinetics. Initial changes are directly related to the growth of the sulfide scale and changes occurring due to this growth. Our results show that the microcrack initiates on the convex surface of samples. To understand microcrack initiation, we will section the exposed

samples to measure the scale thickness and study other morphological changes occurring in the scale for each test condition. We expect to finish this investigation by May 1997.

The second objective to do these tests was to construct an experimental base line for another set of tests required for the DOE/AF&PA database. Published results from various authors and previous tests done at IPST indicate that the presence of smelt can increase the corrosion rates in high temperature gaseous environments. Recovery boiler tubes, during operation, are covered by the frozen smelt whose composition may vary with time and position. Bulk gases have to go through the smelt to the smelt/metal interface for the corrosion reactions to take place. Changes in gas composition due to the reactions of gas with smelt will affect the corrosion characteristics. These data are very important for the recovery boiler corrosivity database; however, very limited smelt data are available in the published literature. Therefore, we have started an experimental program to generate these data and to increase our understanding of the effects of the smelt composition on the corrosion rate of water wall tube materials. Apparatus required for these tests have been modified. Preliminary results from these tests show that the corrosion rate of SA-210 carbon steel is considerably higher when exposed to the 1% H_2S gas passed through the smelt as compared to the tests done without the smelt in otherwise similar conditions. Present series of tests on SA-210 are expected to be complete by July 1997. After finishing our tests on carbon steel, we will do similar tests on the 304-L stainless steel, which is also exposed to similar conditions in the lower furnace.

Long-term kinetics tests are being done to understand the changes in the corrosion kinetics of 1018 carbon steel in 1% H_2S at 400°C for up to 10,000 hours of exposure. Weight changes are recorded at short intervals of time. Last time this test was interrupted after about 2900 hours of exposure as the quartz spring broke. Therefore, we had to start this test again. Test has undergone ~5000 hours of exposure time and will be over in another 5000 hours (~6 months). Results, so far, have shown that the reaction kinetics have changed from the parabolic to linear after about 1500 hours of exposure. Scale characteristics will be studied after the completion of this test.

Ph.D. student (Matt Estes) who is working on the air-port corrosion has finished experiments for his thesis. The goal of his thesis work was to measure the solubility of Cr_2O_3, Fe_2O_3, and NiO in molten salts as a function of the basicity of NaOH. Plots of the chromium ion concentration indicate a minimum solubility at -log $a_{(Na_2O)}$ of 8.2. The data support two mechanisms for dissolution of the Cr_2O_3. The basic dissolution had a slope of -0.988, consistent with the formation of Na_2CrO_4. The acidic dissolution had a

slope of 1.48, consistent with the formation of Cr^{3+}. Within the range of the experiments, iron oxide showed a basic dissolution with no solubility minimum. The basic dissolution found had a slope of -0.51, consistent with the formation of ferrite. Nickel oxide was not very soluble in NaOH. It showed an acidic dissolution with a slope of 1.01, consistent with the formation of nickel ions. With Cr_2O_3, the solubility curve found for KOH was similar to the NaOH curve. The solubility of chromium in KOH was found to be substantially higher than in NaOH. The results from weight loss experiments on chromium metal were then compared to the solubility curves for Cr_2O_3 to confirm that the metal oxide solubility was the rate-limiting step in the corrosion mechanism.

Estes is in process of analyzing his results and writing his thesis. He is expected to defend his thesis by the end of May 1997. The main results from his 1996-97 research are included in this report. Part of his work on the solubility of Cr_2O_3 in molten NaOH has been submitted for publication, and a copy of that paper is incorporated into this report.

Recently, another exploratory project was started to explore the possible stress corrosion cracking (SCC) mechanisms, which can operate on the composite tubes during shutdown conditions. Results of the ORNL investigation and other published results indicate that the composite tube cracking in kraft recovery boilers may be due to SCC. Various possible environments, including different constituents of washwater, will be studied in this project. SCC susceptibilities of different microstructures of stainless steel in the possible recovery boiler environments during the shut down condition will be studied. Part of this project is an A-190 (M.S. research) project for Daniel Andrews-Wilberforce. The initial set of tests using U-bend specimens is already being done. Slow strain rate tests will be carried out to screen the possible wash water constituents, which are capable of causing stress corrosion cracking of stainless steel composite tubes. A systematic study will answer some of the present cracking problems as well as indicate other possible mechanisms of stress corrosion, which can possibly operate in the recovery boiler environments. Knowledge of these mechanisms is important for their successful mitigation and safe operation of the recovery boilers.

Introduction

The main objective of this project is to understand the causes of corrosion on the waterwall tubes in the lower furnace of the kraft recovery boiler. Better understanding of these causes is important to develop successful mitigation strategies. Different types of material-related problems on the fireside have been observed and reported by various mills, and corrosion has been implicated in several smelt-water explosions over the years. Obviously, safe operation of the boiler is of prime concern, so IPST has been aggressively pursuing research, which will contribute to the general, and specific, understanding of recovery boiler corrosion.

The focus of this program is consistent with IPST's goals for its dues-funded research program in that it is longer term with an emphasis on a fundamental understanding rather than a short-term quick fix without any understanding of the underlying reasons for the observed behavior. Parts of this program are leveraged with a large DOE/AF&PA project whose general objectives overlap with some of the objectives of this project. This program is also being leveraged with Ph.D. and M.S. student research projects, with a budget independent of this particular dues-funded project.

Discussion of FY 96-97 Results

This project has been divided into three different tasks to focus our efforts on the areas that need the most attention. Table 1 gives an overview of the structure of the overall program and shows how member dues-funded projects are leveraged with other related activities, such as externally funded projects and student research. Next to each task is a brief description of the main objective or the question that needs to be answered.

Dues-Funded (F018)	*Additional Funding Leverage*
Task 1. Gas Phase Reactions To generate basic understanding of corrosion processes involved in lower furnace environments	DOE/AF&PA Corrosivity Monitoring of Kraft Recovery Boilers
Task 2. Long-term Kinetics To understand long-term kinetic changes in sulfidation of carbon steels	
Task 3. Air-port Corrosion To determine a mechanism to develop efficient mitigation strategy	Ph.D. Student (Matt Estes)
Externally Funded Projects	
DOE/AF&PA Corrosivity Monitoring of Kraft Recovery Boilers	
Exploratory Project/M.S. Student Research	
Stress Corrosion Cracking of Composite Tubes	

The remainder of the report is organized to cover the status of each of the tasks shown in Table 1. The objectives of the DOE project and new project on the composite tube cracking are covered last.

Task 1

Effects of gas phase environment on corrosion rates in simulated recovery boiler lower furnace environments

TASK OBJECTIVE:

(Determined based on needs for data for the corrosion database in DOE/AF&PA project)

1. To study corrosion processes occurring during initial stages of sulfidation of SA-210 carbon steels in AF&PA tests and generate the required data for the database.
2. To establish an experimental base line data for the tests to study the effects of the presence of smelt on the gas phase reactions in a recovery boiler environment.

INTRODUCTION:

Fireside corrosion of kraft recovery boilers is one of the pulp and paper industry's continuing problems. Corrosion may lead to thinning and rupture of the wall tube that results in water/molten salt interaction and subsequent explosion. Iron (in carbon and stainless steel alloys) is converted to iron sulfide by the sulfidation process whose kinetic is the first step toward understanding the corrosion process and estimating the safe operating life of the recovery boiler. The goal of this set of experiments is to understand the initial changes in the kinetics of sulfidation of SA-210 carbon steel, and to set the stage for studying the process with the presence of artificial smelt that simulates the complex environment of the recovery boiler.

EXPERIMENTAL WORK:

The specimens were cut from a two-inch diameter, SA-210 carbon steel tube, and prepared (machined, burnished, etc.) according to AF&PA's test method in the 1995 report. The specimen made that way has, beside the four edge faces, two curved surfaces (inner concave surface and outer convex surface). Testing procedures were similar to the standard AF&PA test method. Two specimens were exposed to a 1% H_2S environment at different temperatures for periods of 4, 8, 24, and 72 hours. Each specimen was weighed before and after the test to record weight change. One specimen was sandblasted to remove the sulfide scale and weighed to give weight loss information, while the other

specimen was stored for future scale examination.

RESULTS AND DISCUSSION:

Results in Figure 1 are weight gain measurements for the SA-210 specimens tested for various time periods at 400°C in a 1% H_2S gas environment. Data points from the previous tests done for 168 hour and 320 hour under similar conditions are also plotted in Figure 1 for comparison. Weight gain increases with the test time, but the change in the kinetics of reaction is not clear from this plot. The data in Figure 1 were replotted on a log-log scale and are shown in Figure 2.The slope in Figure 2 changes from ~0.5 to 1.2 after about 72 hours of exposure. Theoretically, the slope of 0.5 for this type of plot corresponds to a diffusion-controlled step in the reaction, whereas the slope of 1.0 or higher indicates that the rate-controlling step is a chemical reaction. Accuracy of the weight gain measurements depends upon factors such as loss of scale due to spalling or to the procedures of specimen recovery from the furnace, whereas the error in the weight loss measurements may occur due to the cleaning procedure (sandblasting), but error due to the cleaning process is easily controllable. Figure 3 shows weight loss data from the same tests as described in Figures 1 and 2. For this set of experiments, corrosion rates from the weight gain measurements and weight loss measurements are very similar.

In all tests, the scale on the concave surface appeared to be more compact than the one on the convex surface. Furthermore, when the microcracks were present, the scale on the convex surface of the specimen appeared to contain a higher density of cracks than the concave surface. This is important for the waterwall tubes as the convex surfaces are exposed to the fireside corrosion in recovery boilers. With growth, compressive stresses buildup in the scale. Accumulation of growth stresses may eventually result in buckling of the sulfide scale initiating microcracks. Microcracks provide easy access to the metal surface and result in increased reaction rates. Cracks in the sulfide scale cannot heal; however, the product of further sulfidation reaction may cause further growth stresses and initiation and propagation of more cracks. This process eventually may lead to sulfide scale spalling and increases in the corrosion rate.

Similar tests were also conducted at test temperatures of 320°C, 360°C, 440°C, and 480°C, and the results are shown in Figure 4. In each case, the weight change increases with test time. There were changes in the slope for each set of temperatures, but the trends were not very conclusive. The increase in temperature at any given test time showed an increase in weight loss, as is expected. This is better illustrated in Figure 5, where the weight loss is plotted against the test temperature for different test times.

Corrosion rates in mils per year (mpy) were calculated from the weight gain and weight loss measurements for all the tested specimens and are shown in Table I. Figure 6 shows the corrosion rates, calculated from the weight loss measurements, as a function of the test time. It can be seen clearly from the results in Figure 6 that the corrosion rate (averaged over test time) for each tested temperature depends upon the testing time. Dependence is particularly strong for the short test times. Sulfidation of carbon steel under tested conditions follows the parabolic rate law in the initial stages. Therefore, the rate of corrosion decreases with test time until other processes such as microcrack initiation, spalling of scale, or breakaway corrosion triggerin. Results shown in Table I show that the tests done at higher temperatures or for longer times showed a significantly higher number for the weight loss measurement than the weight gain measurement when compared to the tests done at lower temperatures or shorter times. This may be due to spalling of relatively thicker sulfide scale during the test or during retrieval of the sample from the furnace.

These results emphasize on the dangers of using short time tests to predict long term corrosion behavior. Recovery boilers may operate for more than 10,000 hours between routine shutdowns; therefore, knowledge of corrosion processes occurring for those time periods is very important. However, most of the data available to us in published literature is for considerably shorter periods. Results from this study show that to predict long-term behaviors based upon laboratory results, one needs to have a good understanding of the overall processes involved in every stage of the test. This knowledge is even more important to scrutinize the published data for the corrosion database. Further

testing and characterization of sulfide scale is continuing.

CONCLUSIONS:

1. Corrosion rate of SA210 carbon steel increases with increases in temperature for a given test time.
2. Corrosion rates are high in the beginning of the test (~8 hours), after which the rates decrease with time at a steady rate.
3. To successfully predict long-term behavior from a relatively short time test, one has to understand the various processes involved in sulfidation. Definition of "minimum short test time" to predict some "maximum long time" behavior depends upon different processes involved under test conditions (e.g., initial scale growth kinetics, microcrack initiation in scale, scale spalling, and breakaway corrosion, etc.). The role of these processes in the overall corrosion rate needs to be fully understood and taken into account for a successful prediction.

Table I. SA210 tested in 1% H_2S

Spec. #	Temp., °C	Time, hr	Wt. Gain, $g/cm^2 \times 10^{-4}$	MPY	Wt. Loss, $g/cm^2 \times 10^{-4}$	MPY
308	320	4	0.82	15	1.07	20
313			1.08	20		
318		8	1.47	14	1.96	18
319			1.87	17		
322		24	3.82	12		
323			3.91	12	6.11	19
326		72	7.64	8		
327			7.71	8	11.58	12
314	360	4	1.79	33	2.52	46
315			1.81	33		
307		8	2.10	19	2.83	26
312			2.45	22		
305		24	3.33	10	4.99	15
310			3.94	12		
324		72	4.38	5	7.03	7
325			4.79	5		
203	400	4	2.20	40	3.65	67
209			1.86	34		
206		8	2.40	22	6.61	60
201			2.63	24		
225		24	4.82	14	9.66	30
226			4.20	13		
85		72	7.56	8	13.92	14
98			7.44	8		
224		162	17.41	8	26.88	12

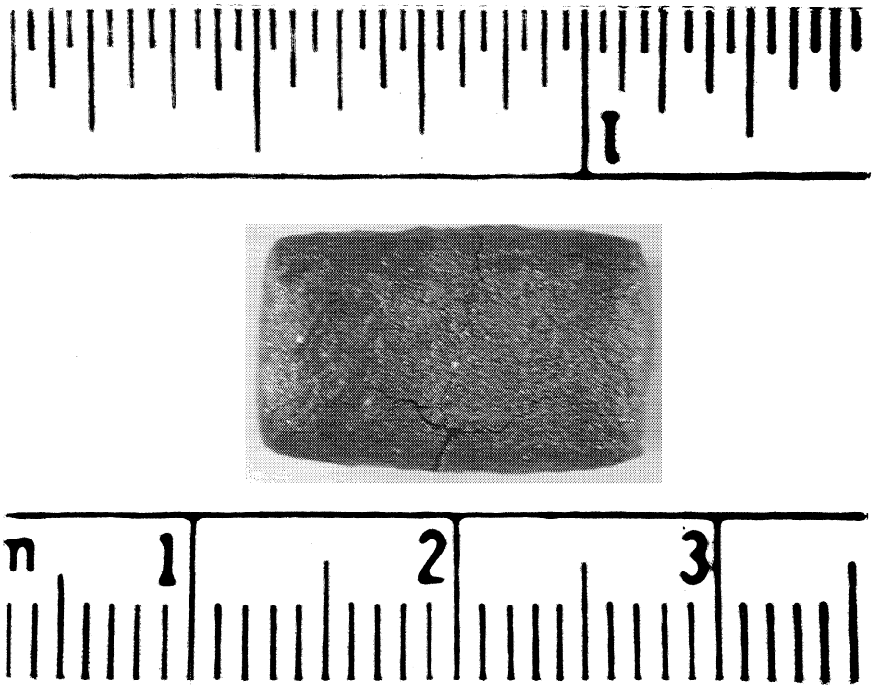

Figure 17. Carbon Steel corrosion products after corrosion in molten smelt at 800°C. Uncoupled

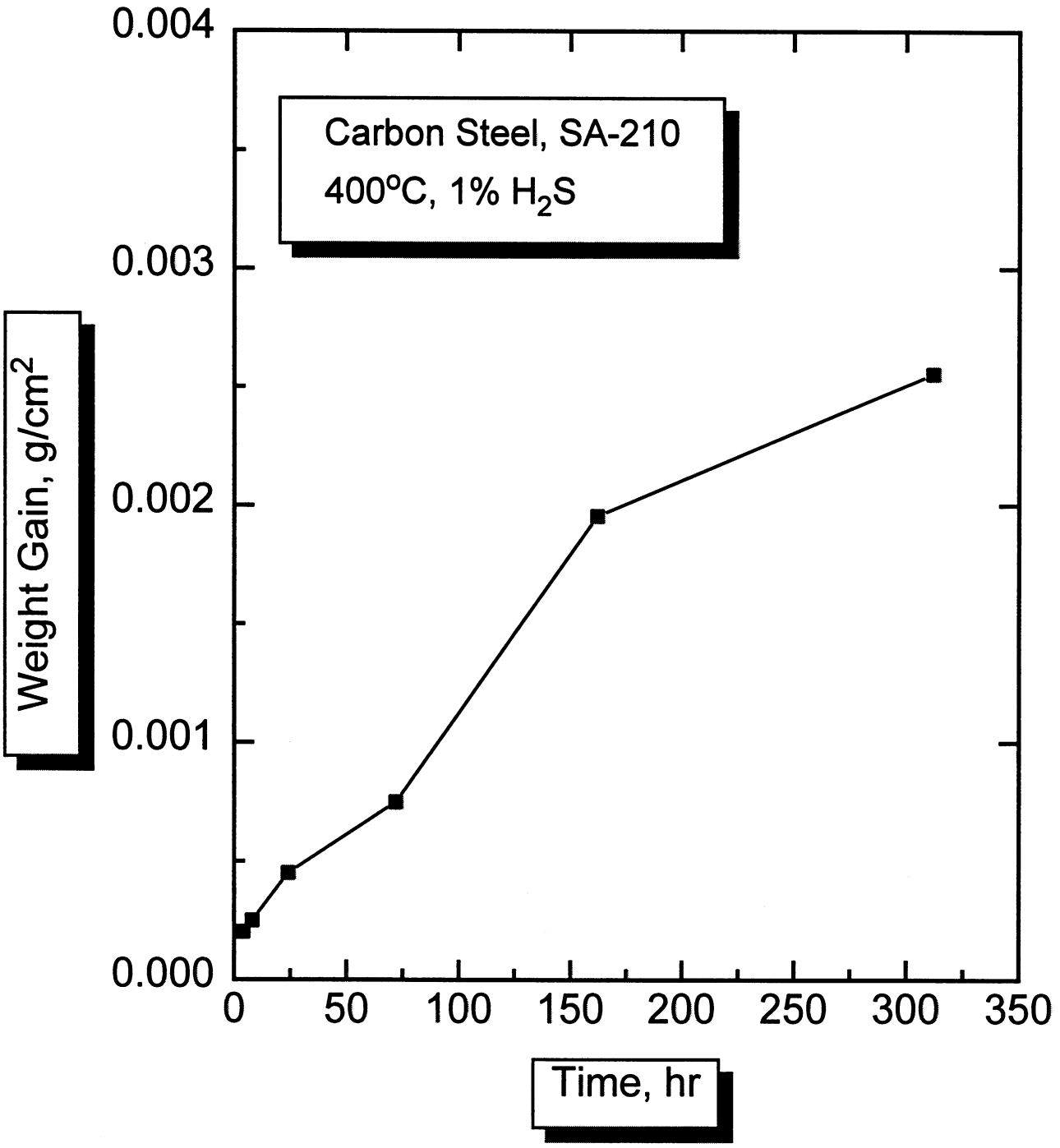

Figure-1. Weight gain as a function of time for SA-210 carbon steel in 1% H_2S at 400°C.

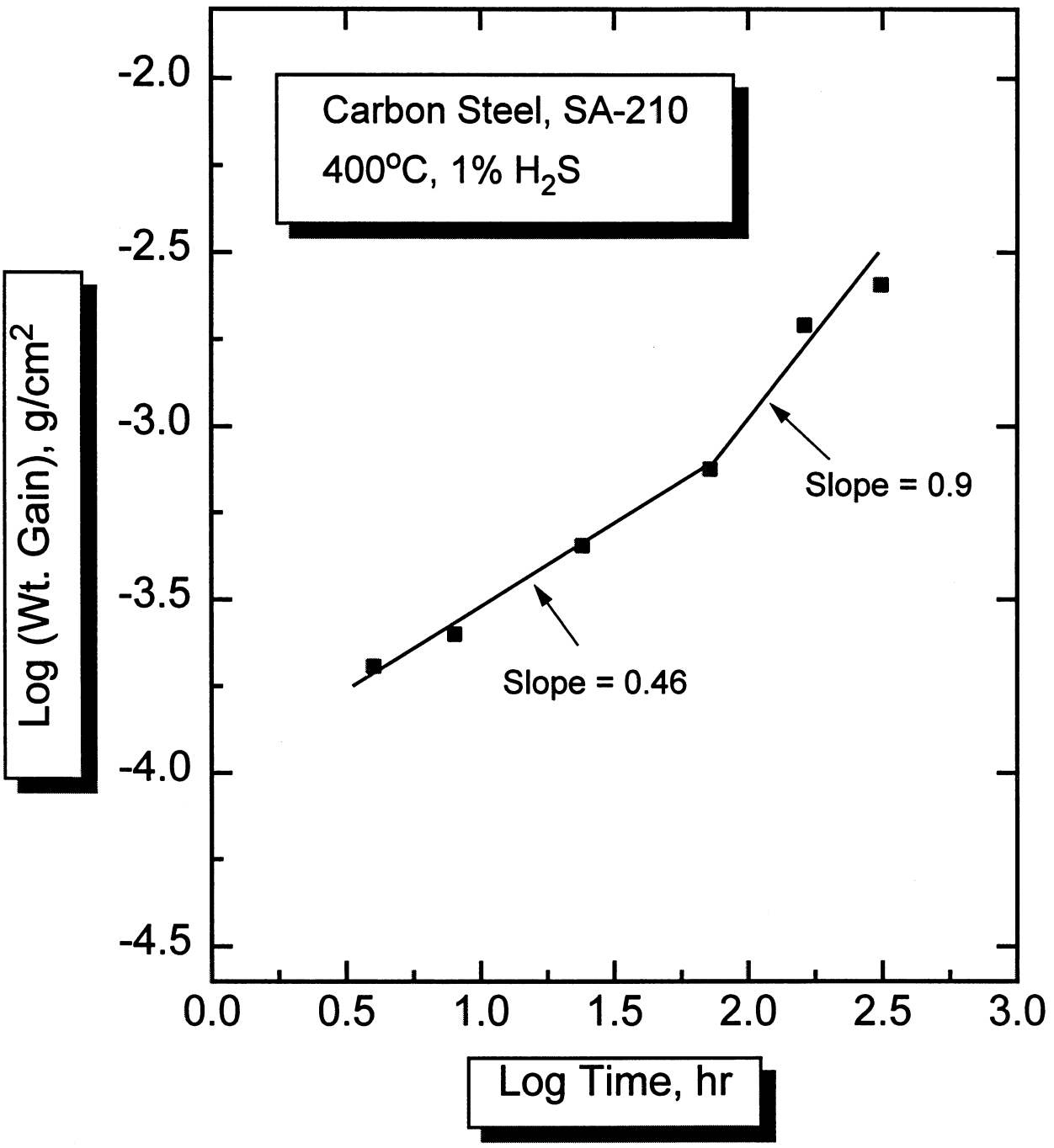

Figure-2. Weight gain for SA-210 carbon steel in 1% H_2S at 400°C.

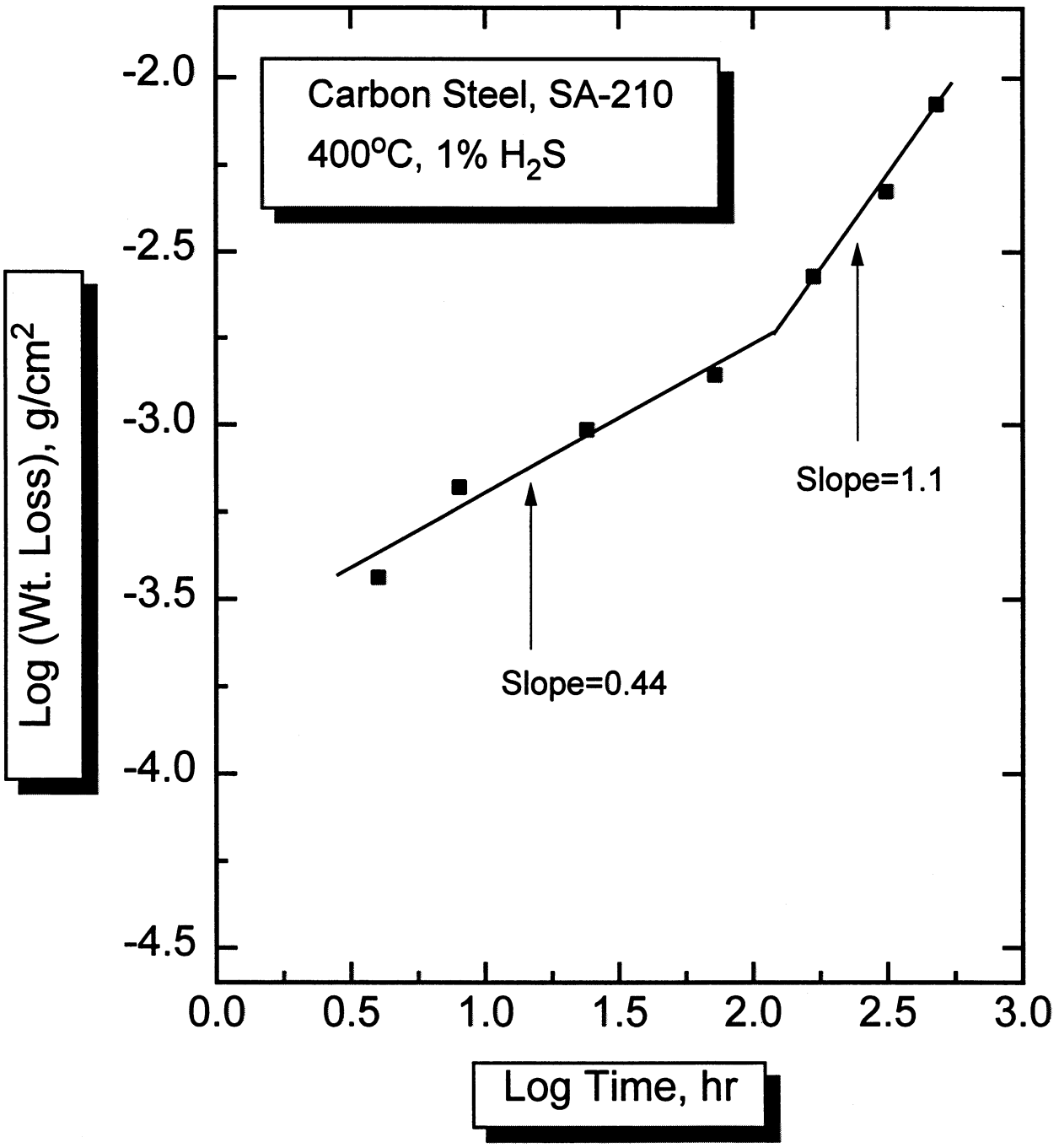

Figure-3. Weight gain for SA-210 carbon steel in 1% H_2S at 400°C.

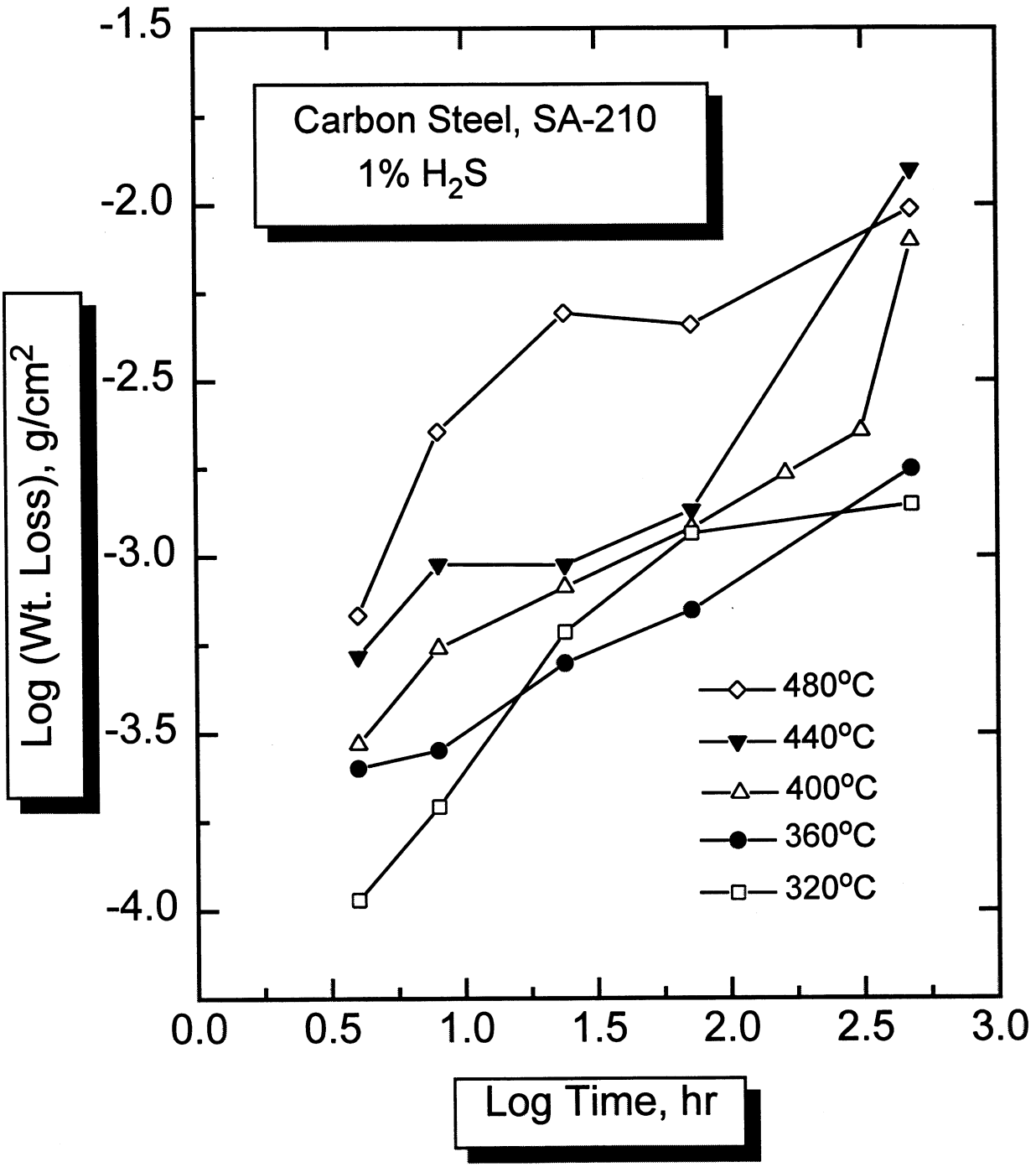

Figure-4. Weight loss for SA-210 carbon steel as a function of time in 1% H_2S.

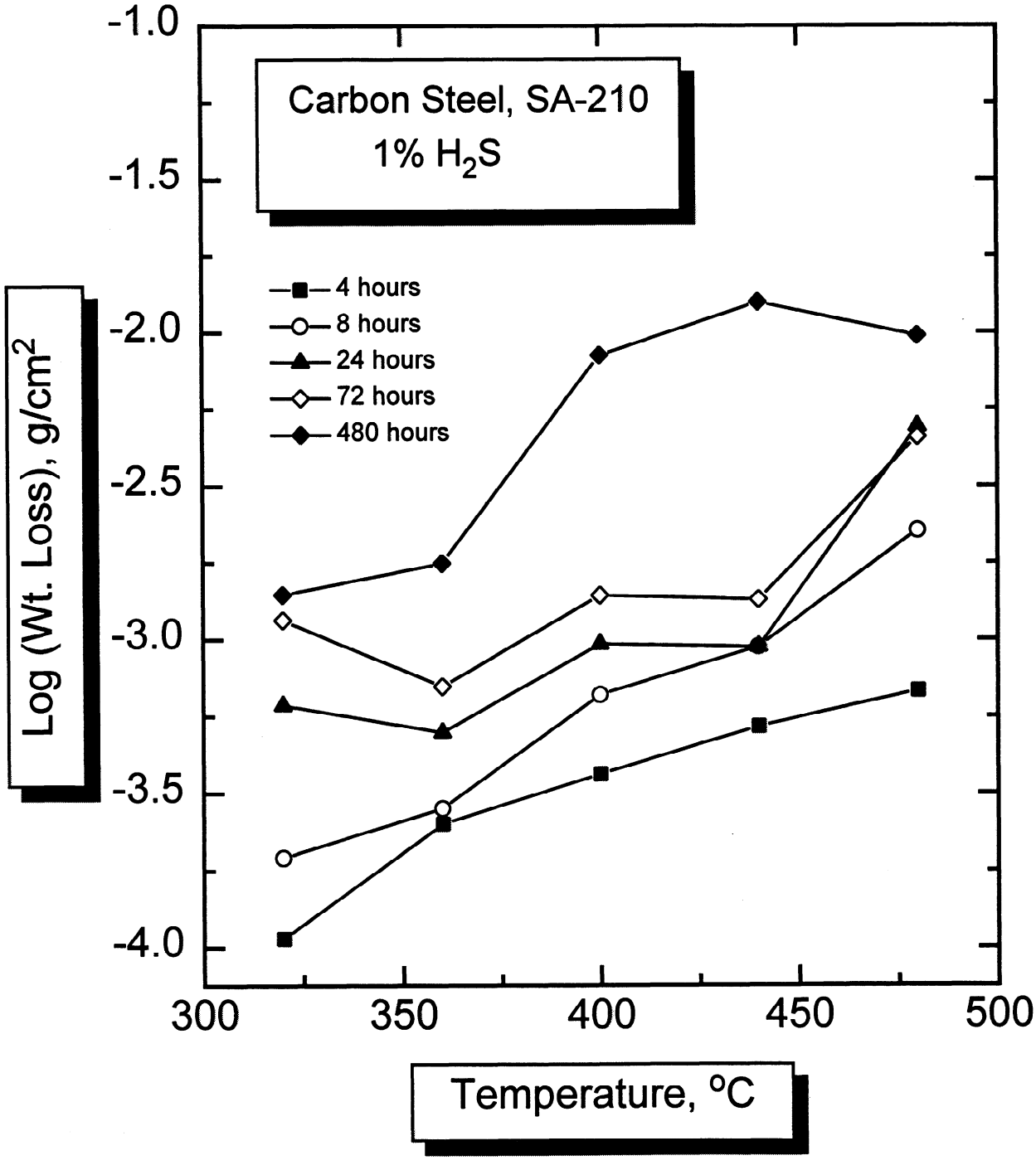

Figure-5. Weight loss for SA-210 carbon steel as a function of temperature.

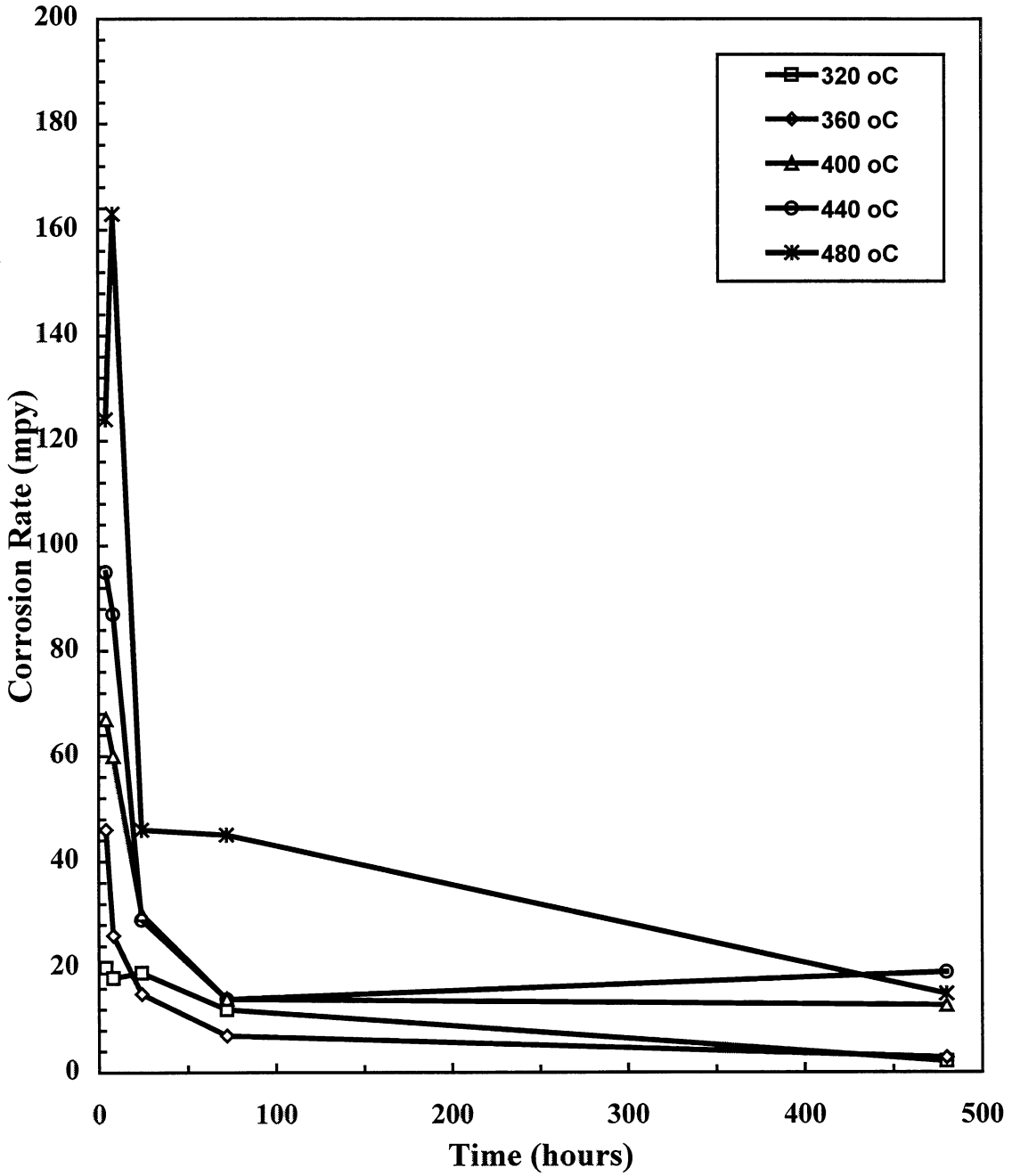

Figure 6. Effect of testing time on corrosion rate of SA210 carbon steel tested in 1% H_2S at different temperatures.

Task 2

Long-Term Kinetics

TASK OBJECTIVE:

To study the long term (10,000 hours) kinetics of corrosion of SA210 C-steel in 1% H_2S at 400 °C

INTRODUCTION:

Boilers are designed to operate for many thousands of hours without replacing waterwall tubes. Even between scheduled shut downs, the boiler must operate for 4000 to 8000 hours, depending upon individual mill maintenance plans. Most of IPST's laboratory tests are at most a few hundred hours and usually much less than that. Alloy rankings are made based upon these short-term experiments as an estimate of remaining alloy life. An implicit assumption in this approach is that the kinetics do not change and the rate laws developed are constant. This has not been demonstrated for this application, and the data generated by discrete weight change measurements show gaps, which need to be better defined if accurate kinetic rate laws are a desired result. Continuous growth of the sulfide scale may result in two scenarios, in one, the growth stresses may increase with increases in the sulfide scale and the scale may spalloff, exposing a bare metal or a thin scale on the surface. In the other scenario, breakaway corrosion may be a result of depletion of the scale-forming element and cause the kinetics to change from parabolic to linear with a higher corrosion rate. This task is designed to determine whether this phenomenon is likely to occur in the recovery boiler environment by making continuous measurements of weight change over a 10,000-hour period.

EXPERIMENTAL PROCEDURE:

As was discussed in previous PAC reports, the upper portion of the Vycor reaction chamber extending above the furnace is now wrapped in heating tape and insulated to ensure that the entire length is above the melting point of sulfur. This was done to avoid condensation of sulfur on chamber walls. A schematic diagram of the experimental arrangement is shown in Figure 7.

Prior to each test, the furnace is burned out to remove any deposits, which may have remained from previous tests. If the Vycor reaction tube is completely clouded over, the tube is replaced with a new one. The new tube is then burned out. A coupon of known surface area is cleaned with acetone and weighed. All coupons are prepared prior to this using the standard procedures discussed previously in PAC reports. The coupon is attached to the platinum chain and then carefully placed into the furnace. The furnace temperature is then slowly raised to the test temperature under a N_2 atmosphere. The coupon is kept under this atmosphere for a short time to allow the quartz spring to come to equilibrium. The flow of test gases is then started. The weight is monitored visually using a cathetometer by measuring the change in spring extension as a function of time. The spring constant of the quartz spring is known, so the weight change can be calculated using Hooke's law.

RESULTS AND DISCUSSION:

Due to delays in receiving additional quartz springs, the long-term test did not begin until August. Results from the first ~5000 hours of test are shown in Figure 8. Results in Figure 8 show a parabolic behavior for the first 1500 hours and a linear rate after that. This test is still running, and more data points will be added to the curve over the next seven months.

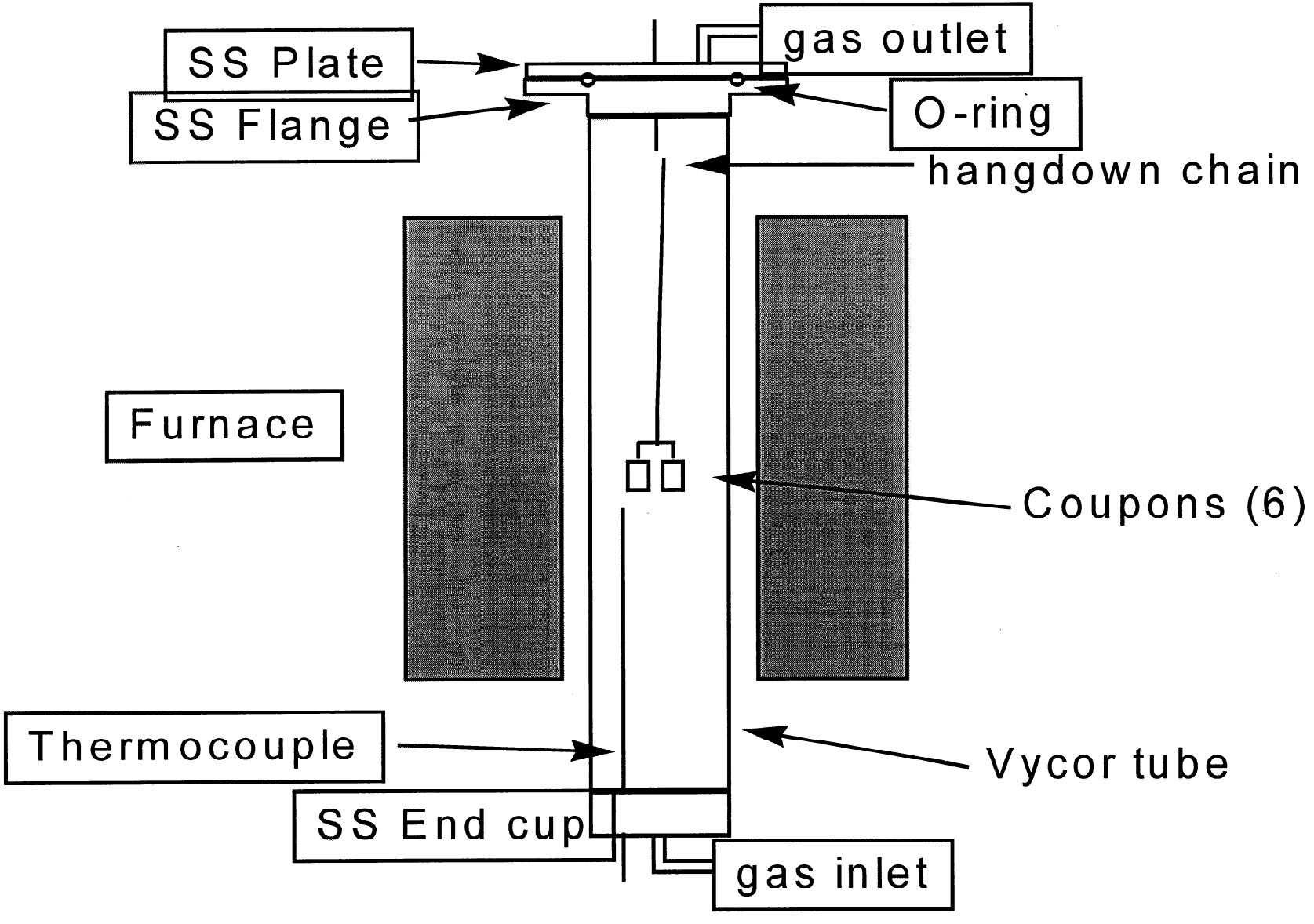

Figure 7. Experimental setup for long-term kinetic tests.

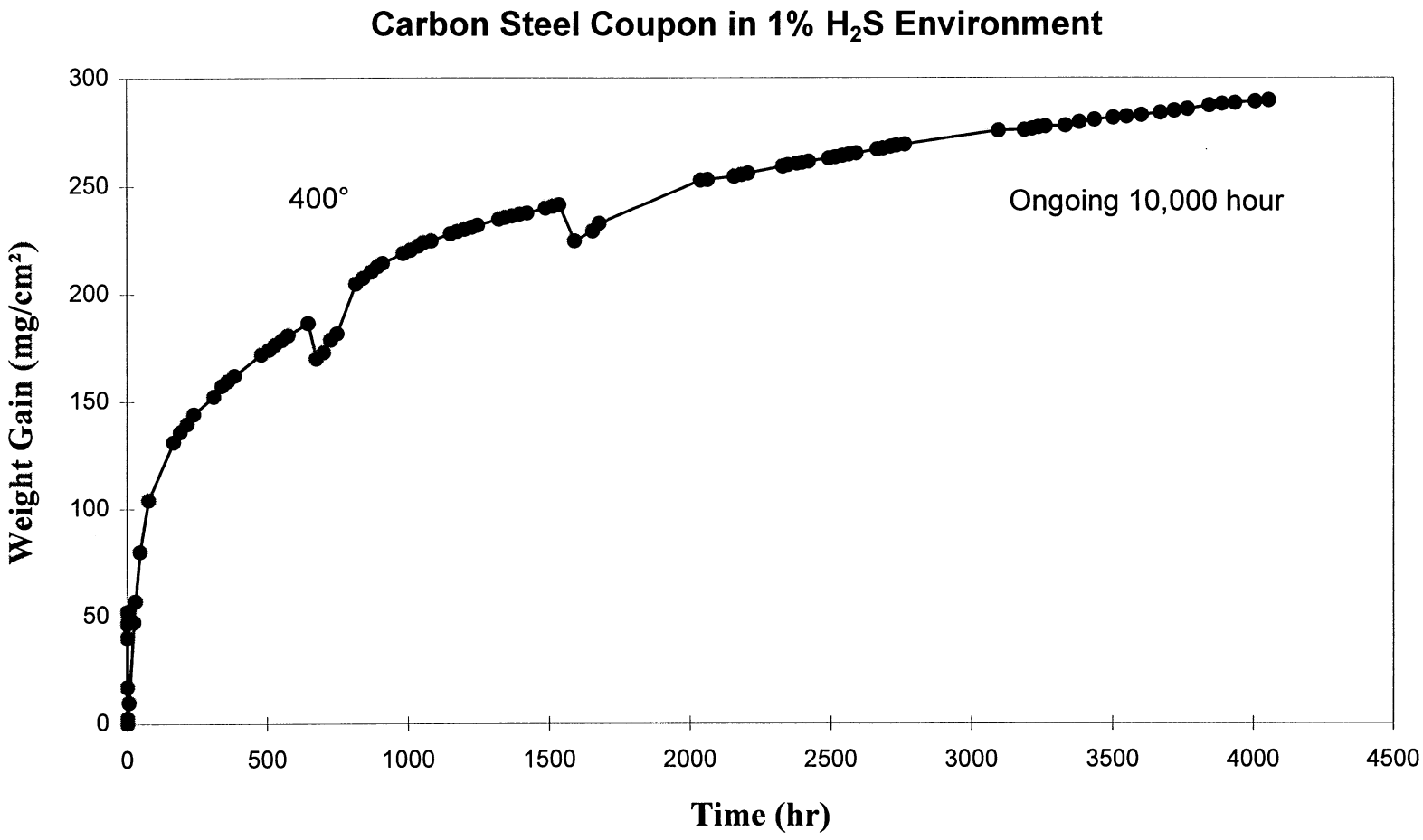

Figure 8. Weight change versus time for the long-term kinetics test.

Task 3

Corrosion of Composite Tube Air-ports in Kraft Recovery Boiler

TASK OBJECTIVES:

To study the solubility of oxides in molten hydroxides.

(Experiments reported here were done by M.J. Estes as partial fulfillment for the Ph.D. degree at the Institute of Paper Science and Technology.)

INTRODUCTION:

The problems of air port corrosion, the theory related to molten salt corrosion, and the equipment and methods used have been described in previous PAC reports, so it is omitted here for the sake of brevity. A copy of a paper submitted to the AIChE Forest Products Division is included at the end of this report, and provides much of the background materials about the theory and equipment and methods. The information provided here is a summary of the completed solubility curves and supporting weight loss experiments.

RESULTS AND DISCUSSION:

Solubility of Cr_2O_3 in Molten NaOH

The basicity vs. solubility plot of chromium oxide is shown in Figure 9. Each basicity condition shown in Figure 1 is an average of three values. Equilibrium was ensured at a given basicity by measuring the concentration of metal ions until it did not change over three days. Chromium oxide was found to have a minimum solubility at a basicity of 8.2. The solid line represents the least squares fit of the data. Basicity error bars were estimated at -log $a_{(Na_2O)} \pm 0.1$ and are mostly due to instrument fluctuation. The error bars on the concentration of chromium were calculated as one standard deviation of the data.

If the basic dissolution reaction is assumed to be:

$$Cr_2O_3 + 2\ O^{2-} + \frac{3}{2} O_2 = 2\ CrO_4^{2-} \qquad (1)$$

At constant $P(O_2)$,

the theoretical slope for the reaction is given by:

$$\left(\frac{-\log CrO_4^{2-}}{-\log O^{2-}}\right) = -1 \qquad (2)$$

The measured value of -0.9879 is in very good agreement with theory. Thus, the melt was yellow in color, which is consistent with the formation of chromate.

If the acidic dissolution reaction is assumed to be:

$$Cr_2O_3 = 2\ Cr^{3+} + 3\ O^{2-} \qquad (3)$$

The theoretical slope for the reaction is given by:

$$\left(\frac{-\log Cr^{3+}}{-\log O^{2-}}\right) = \frac{3}{2} \qquad (4)$$

The measured value of 1.477 is in very good agreement with theory. Thus, the melt was green in color, which is consistent with the formation of chromium ions.

Solubility of Fe_2O_3 in Molten NaOH

The basicity vs. solubility plot of iron oxide is shown in Figure 10. Within the basicity range of these experiments, iron oxide was not found to have a solubility minimum. The negative slope of the line indicates that basic dissolution occurs for iron.

If the basic dissolution reaction is assumed to be:

$$Fe_2O_3 + O^{2-} = 2\,FeO_2^- \qquad (5)$$

The theoretical slope for the reaction is given by:

$$\left(\frac{-\log FeO_2^-}{-\log O^{2-}}\right) = -\frac{1}{2} \qquad (6)$$

The measured value of 0.51 is in very good agreement with theory. Thus, the melt was red in color, which is consistent with the formation of iron ions.

Solubility of NiO in Molten NaOH

The basicity vs. solubility plot of nickel oxide is shown in Figure 11. Nickel metal is known to be resistant to corrosion in molten NaOH. Therefore, it is not too surprising that there is little solubility from a basicity value of 6.8 to 8.4. Nickel oxide only becomes soluble under acidic conditions.

If the acidic dissolution reaction is assumed to be:

$$NiO = Ni^{2+} + O^{2-} \qquad (7)$$

The theoretical slope for the reaction is given by:

$$\left(\frac{-\log Ni^{2+}}{-\log O^{2-}}\right) = 1 \qquad (8)$$

The measured value of 1.05 is in very good agreement with theory. Thus, the melt was a weak green-gray color, which is consistent with the formation of nickel ions.

Figure 19. Stainless Steel corrosion products after corrosion in molten smelt at 800°C. Uncoupled.

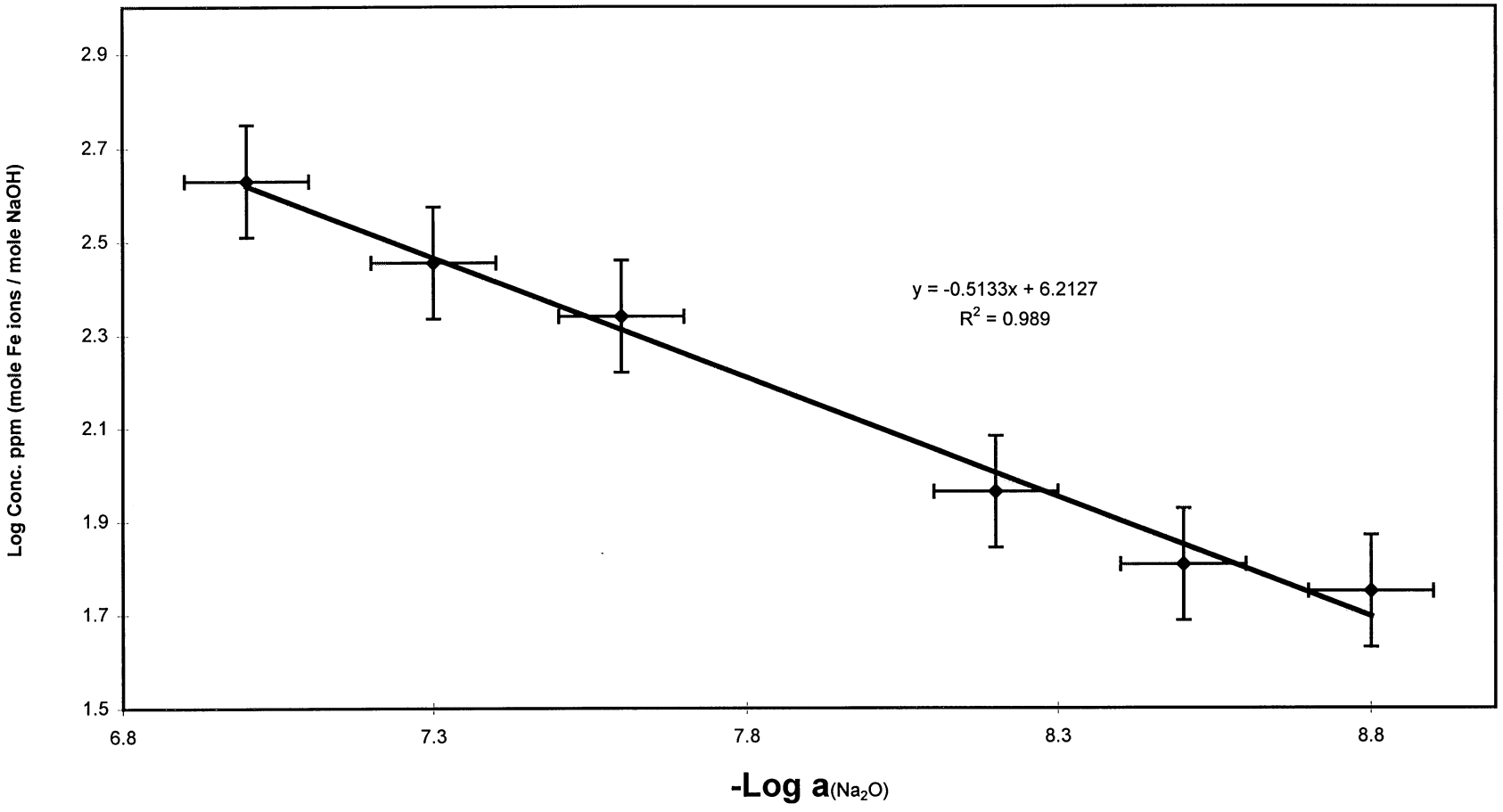

Figure 10. Solubility of Fe_2O_3 in NaOH.

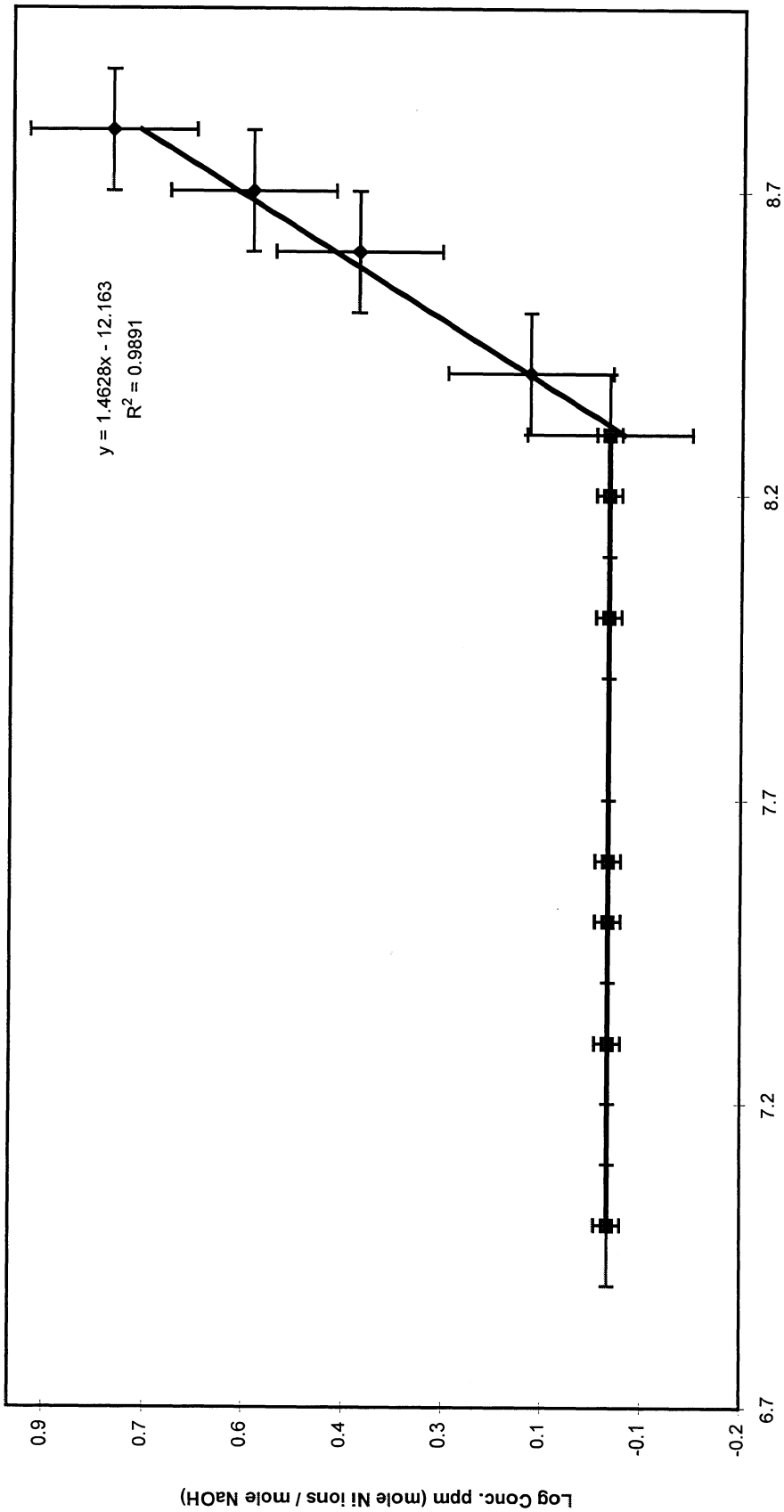

Figure 11. Solubility of NiO in NaOH.

Solubility of Cr_2O_3 in Molten KOH

The effect of KOH was studied because, in laboratory experiments, the addition of KOH to NaOH accelerates the corrosion rate of type 304L stainless steel. For example, a 20% addition of KOH to NaOH caused a 200% increase in the corrosion rate of stainless steel over a 24-hour period (1). The increase in corrosion rate is thought to result from increased solubility of the metal ions. A higher solubility allows more metal ions to enter the solution thereby increasing the corrosion rate.

The basicity vs. solubility plot of chromium oxide in KOH is shown in Figure 12. Experiments with KOH used the same environmental conditions as with NaOH. The minimum solubility was measured at the same basicity value of 8.2 ± 0.1 in NaOH and KOH. As sodium oxide or water vapor was added, the concentration of chromium increased rapidly. The shapes of the lines are similar. For KOH, the basic slope is -1 with the formation of yellow chromate, and the acidic slope is -2.5 with the formation of green chromium ions.

The solubility of Cr_2O_3 in molten KOH increased substantially as predicted. Under basic conditions, KOH had values averaging 300% higher than NaOH. Under acidic conditions, KOH had values 2000% higher at a basicity value of 8.2 that increased to 6000% higher at a basicity value of 8.8. The increase in solubility could account for the 200% increase in the corrosion rate observed in the lab. In conclusion, the solubility of chromium oxide is higher in KOH than NaOH.

Weight Loss Experiments

Weight loss experiments were performed using chromium metal in molten NaOH at basicity values of 8.2, 6.8, and 8.8. The three basicities selected represented the solubility minimum, a basic dissolution, and an acidic dissolution respectively. Figure 13 shows the results of the weight loss performed at the different basicities.

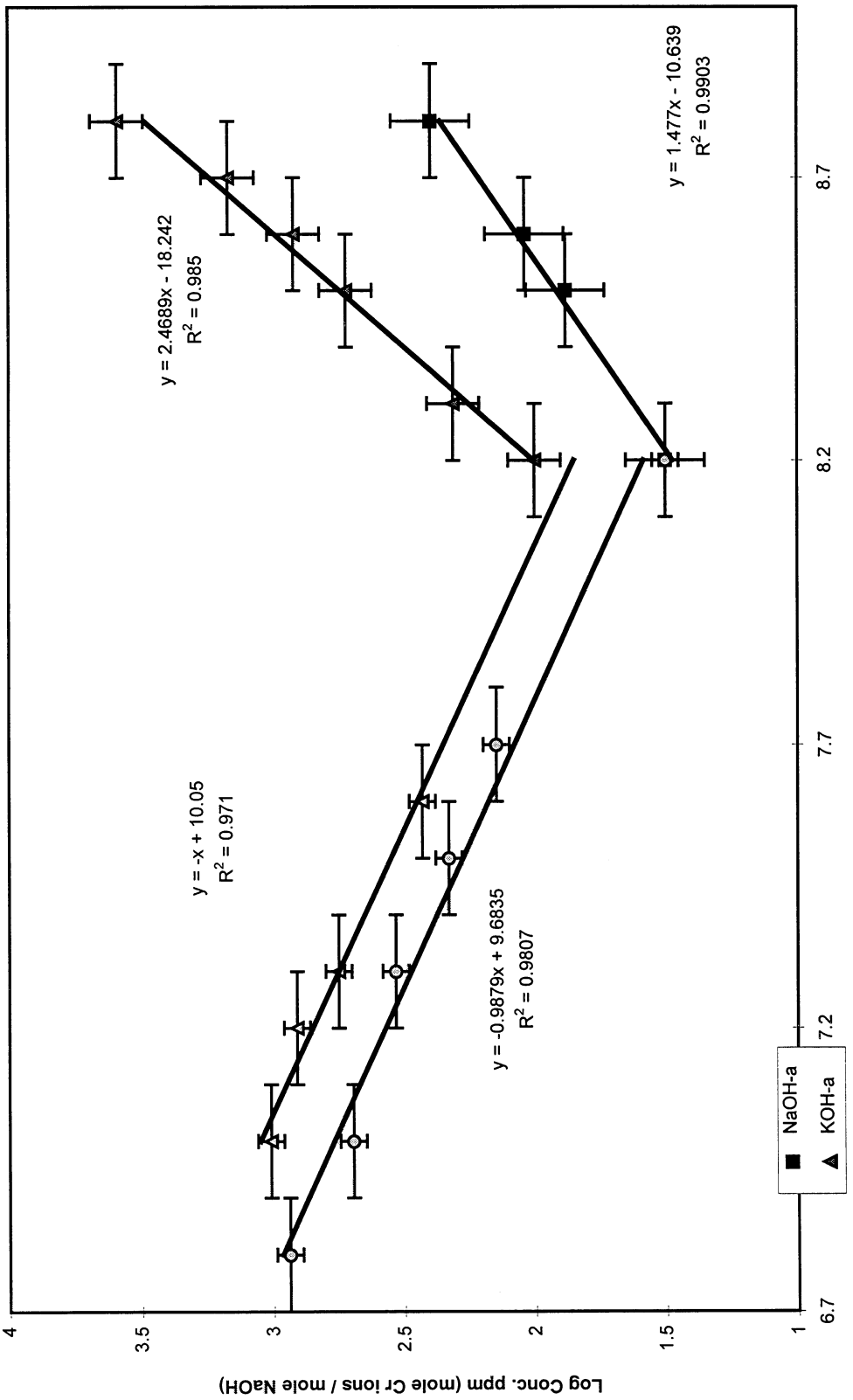

Figure 12. Solubility of Chromium oxide in NaOH and KOH.

The weight loss can be predicted from the basicity and solubility curves. The chromium oxide solubility results in Figure 12 show that the solubility was at a minimum at a basicity value of 8.2. The weight loss of chromium metal is also low at a basicity value of 8.2.

At basicities of 6.8 and 8.8, the solubilities were much higher, which should lead to higher weight loss. Furthermore, the weight loss at a basicity value of 6.8 should be higher than at 8.8 based upon the solubility curve in Figure 12. Weight loss experiments with chromium metal at basicities of 6.8 and 8.8 in Figure 13 showed the predicted increase in weight loss. Therefore, basicity, which determines solubility, does affect the weight loss of chromium metal.

In addition, three samples of chromium metal were placed in NaOH at a basicity value of 8.2. The minimum solubility of chromium oxide was chosen to determine the effect of time on weight loss. After 15 days, the samples were removed and cleaned with water to remove excess NaOH. The samples were then ultrasonically cleaned for 5 minutes in acetone and dried in a dessicator before weighing. The same samples were replaced in the furnace with fresh NaOH for an additional 15 days. The results were graphed showing the weight changes of three trials for 15-day intervals in Figure 14.

Samples taken from the melt were analyzed by the ICP. The samples were yellow, indicating the presence of chromate, so the basicity was slightly on the basic side of the minimum. The average results are summarized in Table 1.

Table 1. Analysis for chromium by ICP.

	Log chromium (ppm)
1st 15 days	2.70
2nd 15 days	1.18
3rd 15 days	0

The results show that the weight loss dropped by half each time a new trial began. The chromium ions in the melt also dropped identically by half until no chromium was detectable.

The kinetic reaction is a first-order reaction. Visually, a dark green, fairly compact scale formed on the test pieces that was strongly adherent to the metal. Because the chromium oxide was minimally soluble in NaOH under the tested conditions, the chromium oxide was able to form a passive layer, which reduced the rate of corrosion. Because the melt was replaced at each 15-day interval, the drop in corrosion rate was not due to the melt becoming saturated.

Conclusion:

The solubility of Cr_2O_3, Fe_2O_3, and NiO was determined as a function of basicity. Chromium oxide was found to have a minimum solubility at -log $a_{(Na_2O)}$ of 8.2. The data suggest two mechanisms of dissolution of chromium oxide in molten NaOH. Basic dissolution (basicity values < 8.2) formed chromate, and acidic dissolution (basicity values > 8.2) formed chromium ions. Iron oxide only underwent basic dissolution, and nickel only underwent acidic dissolution. Curves with potassium were substantially higher in solubility. The higher solubility could account for the higher weight loss observed with the addition of potassium. The solubility curves successfully predicted the weight loss of chromium metal. Chromium coupons at -log $a_{(Na_2O)}$ of 8.2, which is the minimum solubility of chromium oxide in NaOH, developed a green film that successfully lessened the corrosion.

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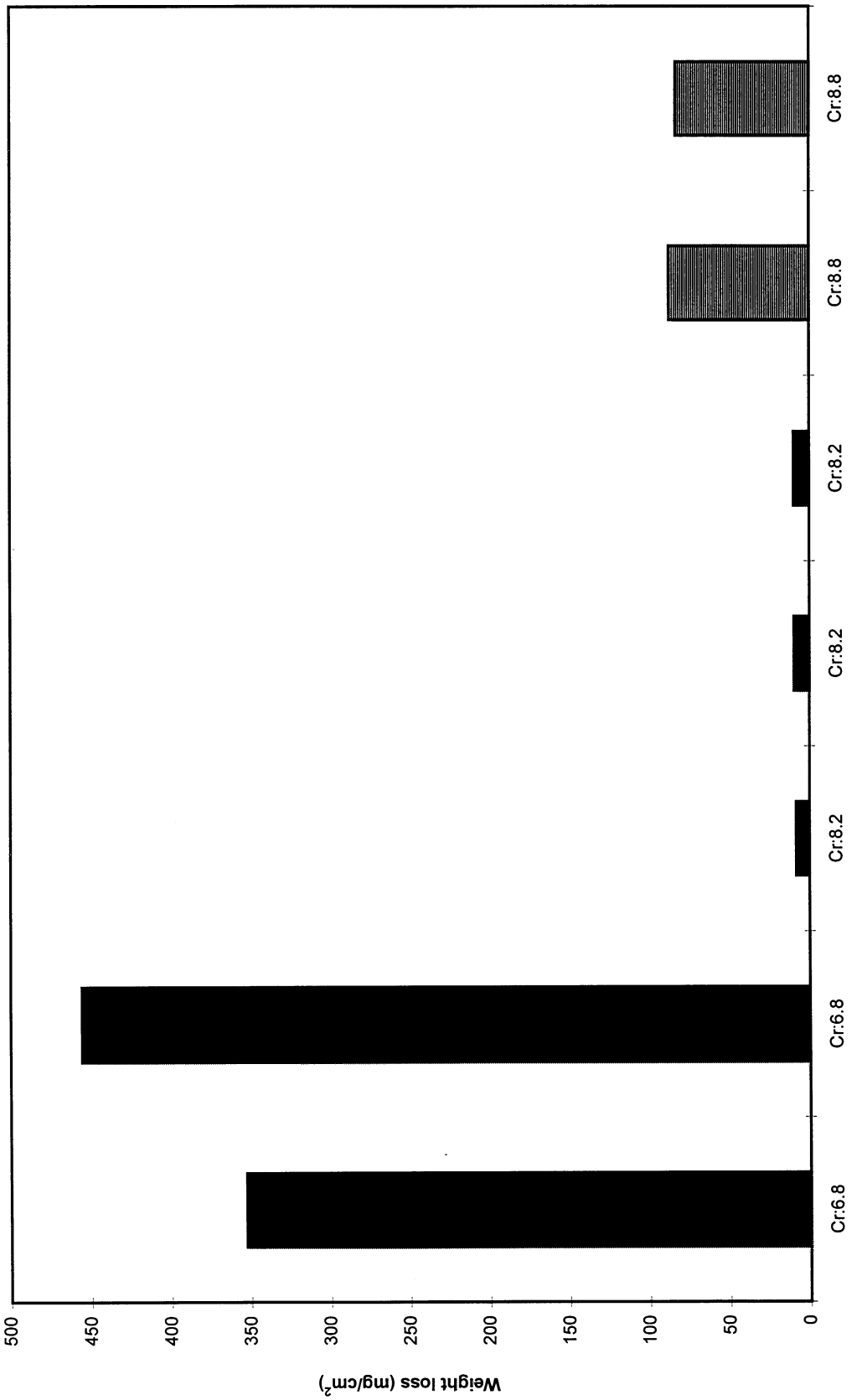

Figure 13: Chromium weight loss in NaOH at 500°C.

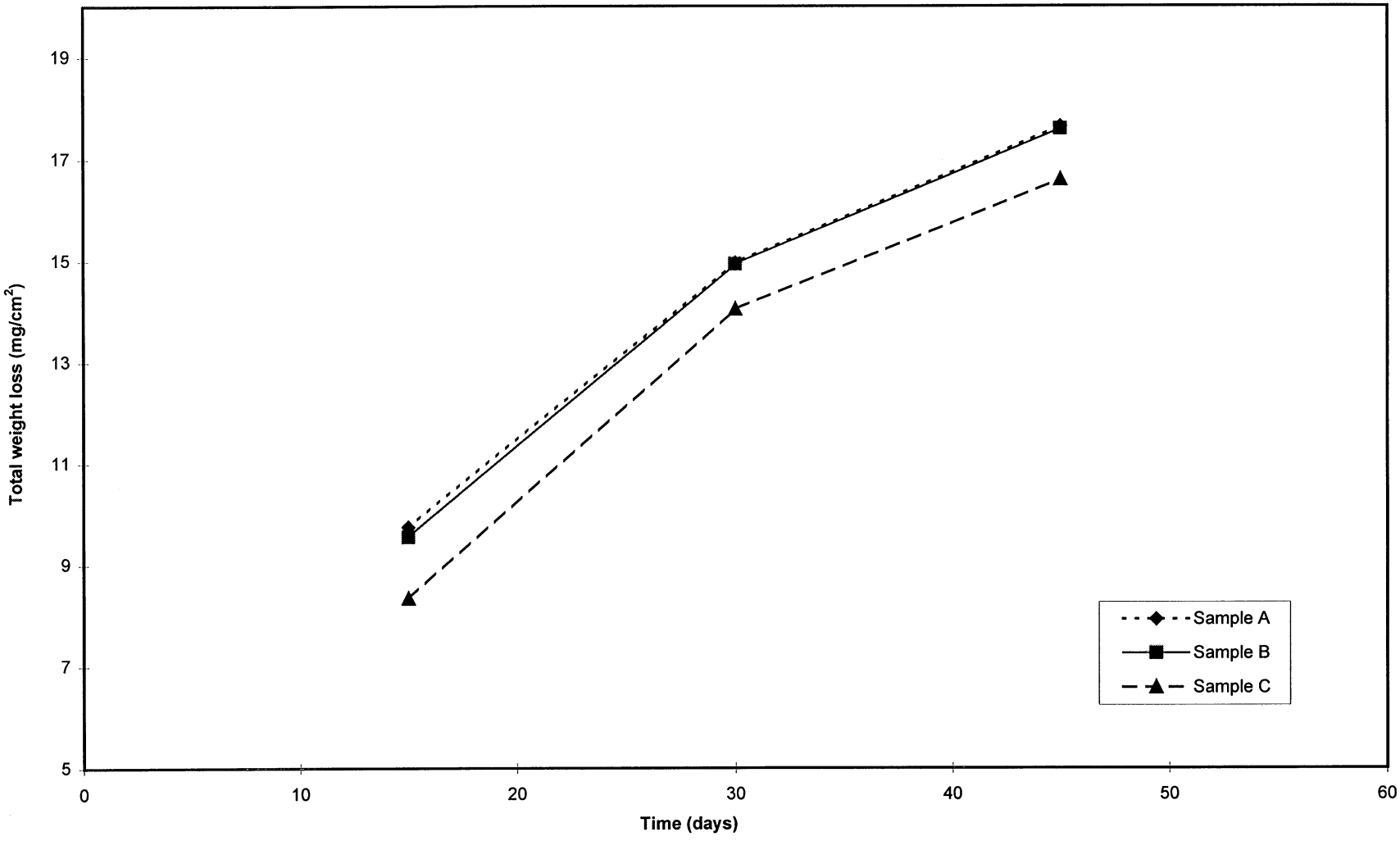

Figure 14. Weight loss as a function of time for Cr in NaOH at a basicity value of 8.2 at 500°C.

Corrosivity Monitoring of Kraft Recovery Boilers

Technical Program Review

External DOE Contract

Project Title: Corrosivity Monitoring of Kraft Recovery Boilers

Project Staff: P. Singh, G. Fonder, S. Al-Hassan

Subcontractors: PPRIC, Battelle

Project Funding: DOE (Cost-share:- AF&PA, PPRIC, IPST)

OBJECTIVES :

The focus of this DOE/AF&PA funded project is to develop an extensive corrosion kinetics database as well as identify or develop a technology to measure corrosivity of an operating kraft recovery boiler. The benefit of such an approach may allow operators to predict or explain the impact of decisions prior to damaging boiler components. The project is divided into four phases. Each phase is designed to last for one year, with the phases as defined in our original proposal to DOE outlined below:

Phase I (1995-96): Feasibility

This first phase has been designed to determine the feasibility of this concept. Initial efforts will be focused on establishing the state-of-the-art of possible measurement techniques. In addition, existing sulfidation and oxidation data will be evaluated by considering databases, which have been constructed for other industries. It is already known that there are gaps in knowledge with certain materials of interest here, so sulfidation kinetics tests will be conducted in common gases.

Phase II (1996-97): Engineering Development

At the successful conclusion of Phase I, more detailed studies on the most promising candidates for corrosion measurements will be undertaken. In addition, the database format developed in Phase I will be used to compile the information which is available in the literature. Additional corrosion tests in more specific environments will also be completed to collect the data needed for establishing limits of use.

Phase III (1997-98): Proof-of-Principle Testing

A series of small-scale experiments will be conducted in a laboratory furnace to test the efficacy of the measurement system developed in Phase II. Tests under closely controlled conditions will simulate as closely as possible a range of actual boiler environments. From these measurements, the database will be used to estimate the corrosion rates and then compare them with actual weight-loss coupons placed in the test rig.

Phase IV (1998-99): Demonstration and Commercial Application

In partnership with an industrial supplier and a mill, the measurement device and corrosion probes will be installed in an operating boiler for comparison. During scheduled outages, careful thickness measurements on an actual boiler will be made to correlate with the model predictions. Alternatively, a special panel may be installed in a boiler for analysis at a particular service interval.

PROJECT STATUS:

The project is divided into three major tasks. Figures 15 and 16 show the organization of this project and various proposed steps to achieve the project objectives. A brief objective statement and the present status of tasks 1 and 2 are discussed separately in the following sections.

Task 1 Development of a Corrosion Kinetics Database (IPST is Task Leader)

Work on this task involves collection of data from refinery, coal gasification, and pulp and paper industry studies, as well as from other fundamental studies to develop a consistent database that can be used by the industry. During the course of developing this database, we have identified that there are some gaps in the data, which are useful to the kraft recovery boilers, so experimental efforts are initiated to collect this necessary data. Experimental work described under Task 1, of the member dues-funded project, is also supported by this project.

Current Status:

At the December 1996 TAG meeting, it was suggested that a more systematic literature search should be done using on-line databases. We started doing a systematic literature search using on-line databases such as METADEX, Chemical Abstracts, and Corrosion Abstracts. So far we have found more than 700 possible titles in the relevant areas from METADEX™, Conferences and Meetings database, and other databases. We are in the process of acquiring these articles, which are not available at IPST or Georgia Tech, as well as further scrutiny of these articles. Since the last TAG meeting in Atlanta, the database has been further modified to incorporate some of the suggestions from that meeting. Chlorine gas has been included as an option. All macros have been converted to Visual Basic Applications (VBA) procedures to refine to database design.

One of our furnaces has been modified to do experiments with smelt experimental procedures, and initial results are discussed in the next section. These experiments will provide us with the required data on the effect of smelt composition on corrosion rates of relevant materials in the kraft recovery boiler environment. Other tests without smelt to fill some important gaps in our database are also being done at IPST and PPRIC.

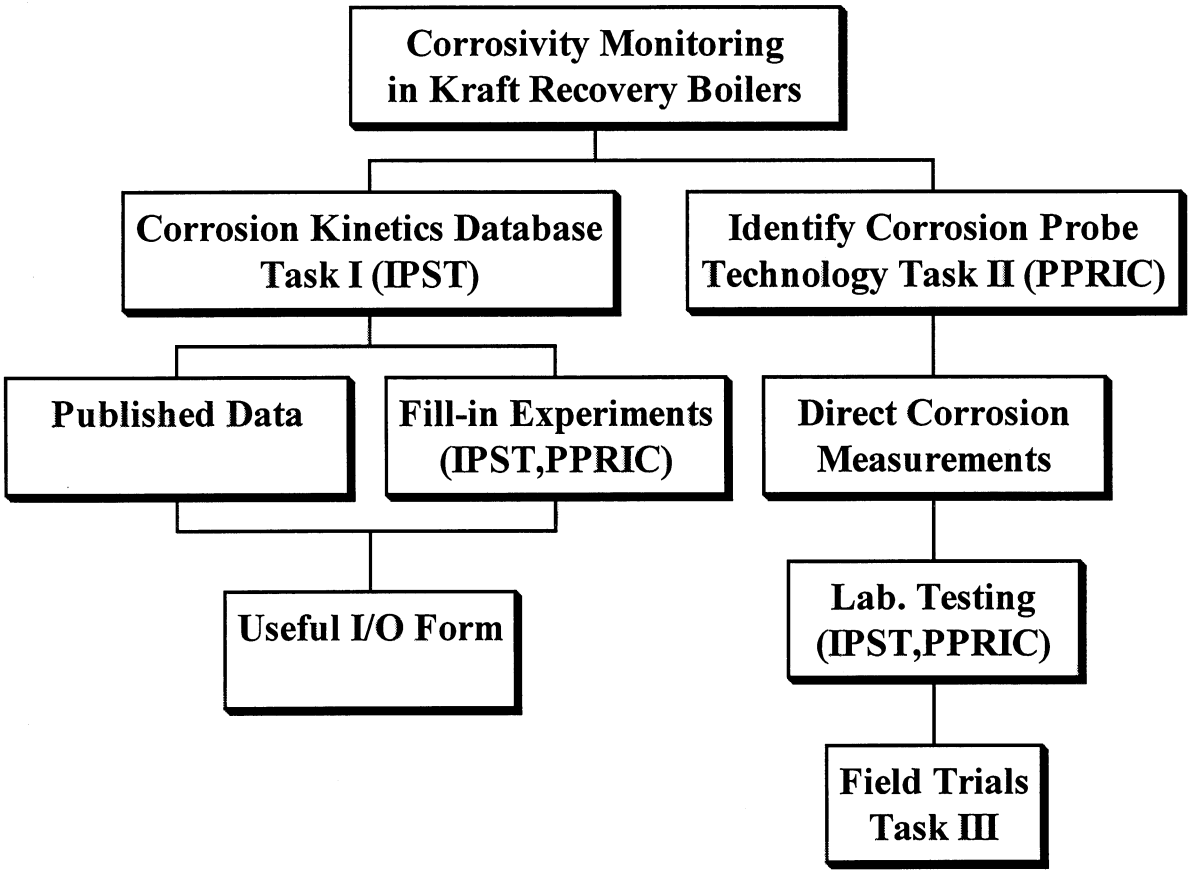

Figure 15. Organization chart showing different tasks of this project.

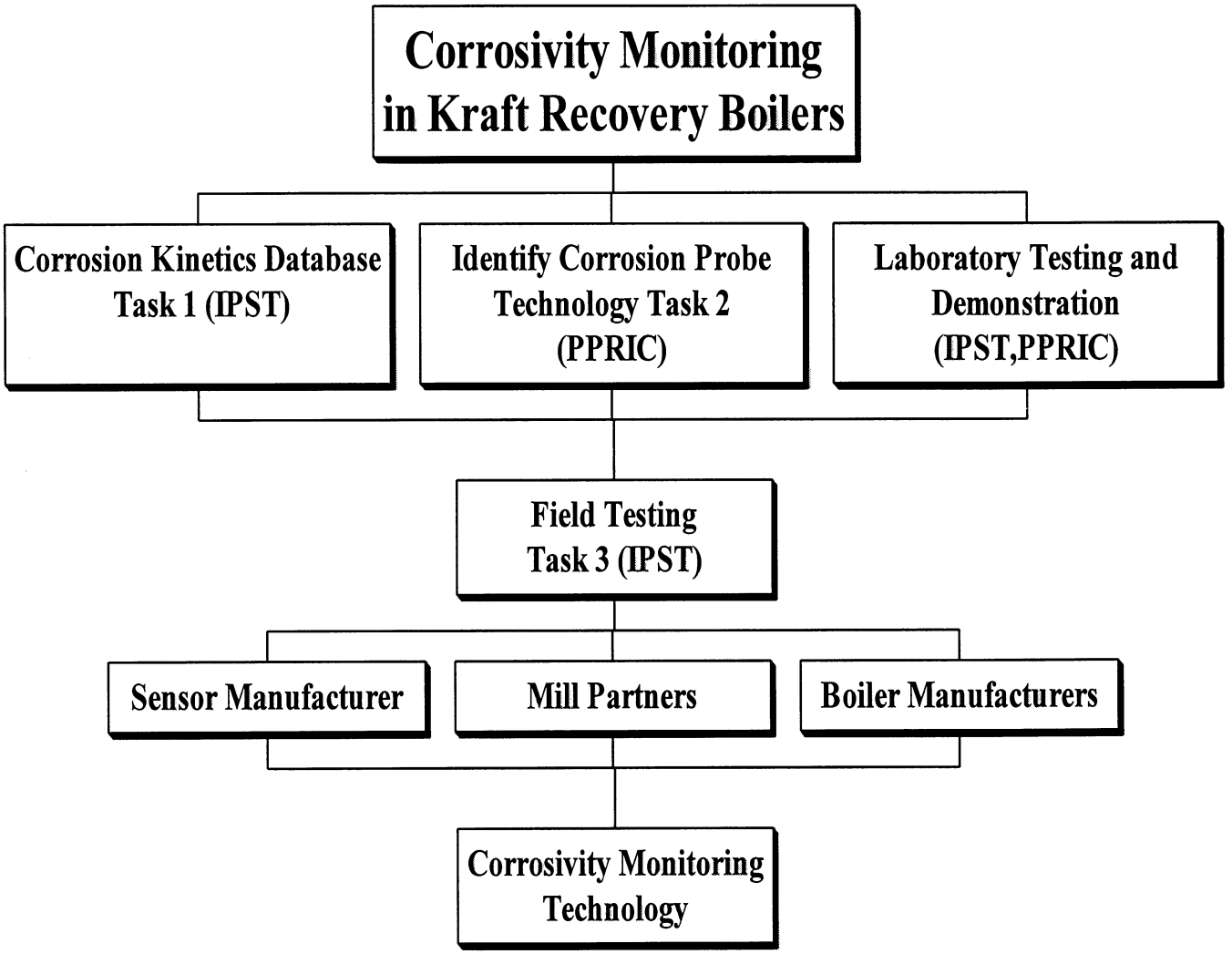

Figure 16. Organization chart showing overall plan of this project.

EXPERIMENTS REQUIRED FOR DATABASE

Objectives: To identify and generate required data for the corrosion kinetics database. (Effects of Smelt Composition on Corrosion of SA210 in Lower Furnace Kraft Recovery Boiler).

Introduction:

This section describes the experimental work done to fulfill the objectives of generating the required understanding and data for the corrosion kinetic database. This objective also overlaps with the general objective of the member dues project of understanding corrosion mechanisms in gaseous environments in the recovery boilers. Previous work has indicated that the presence of smelt changes the corrosion rate and corrosion characteristics considerably in typical recovery boiler environments. There are limited published data available to show these effects in the recovery boiler environments. Thermodynamic calculations have shown that the gas compositions at the smelt/metal interface can be significantly different from the bulk gas compositions in kraft recovery boilers.

Schematic diagram of the apparatus used for these studies is shown in Figure 17. The test furnaces are similar to the ones used for gaseous corrosion studies; however, the smelt containers have been introduced into gas feed lines so that the initial gas mixtures pass through the smelt of a given composition. The smelt containers and the gas lines are kept at the test temperature. Figure 18 shows initial results from these tests, which indicate a higher weight gain or corrosion rate for the SA210 C-steel specimens tested in 1% H_2S at 400°C with smelt when compared to similar tests done without the presence of smelt. Further testing is continuing, and we expect to finish the bulk of these experiments by July 1997.

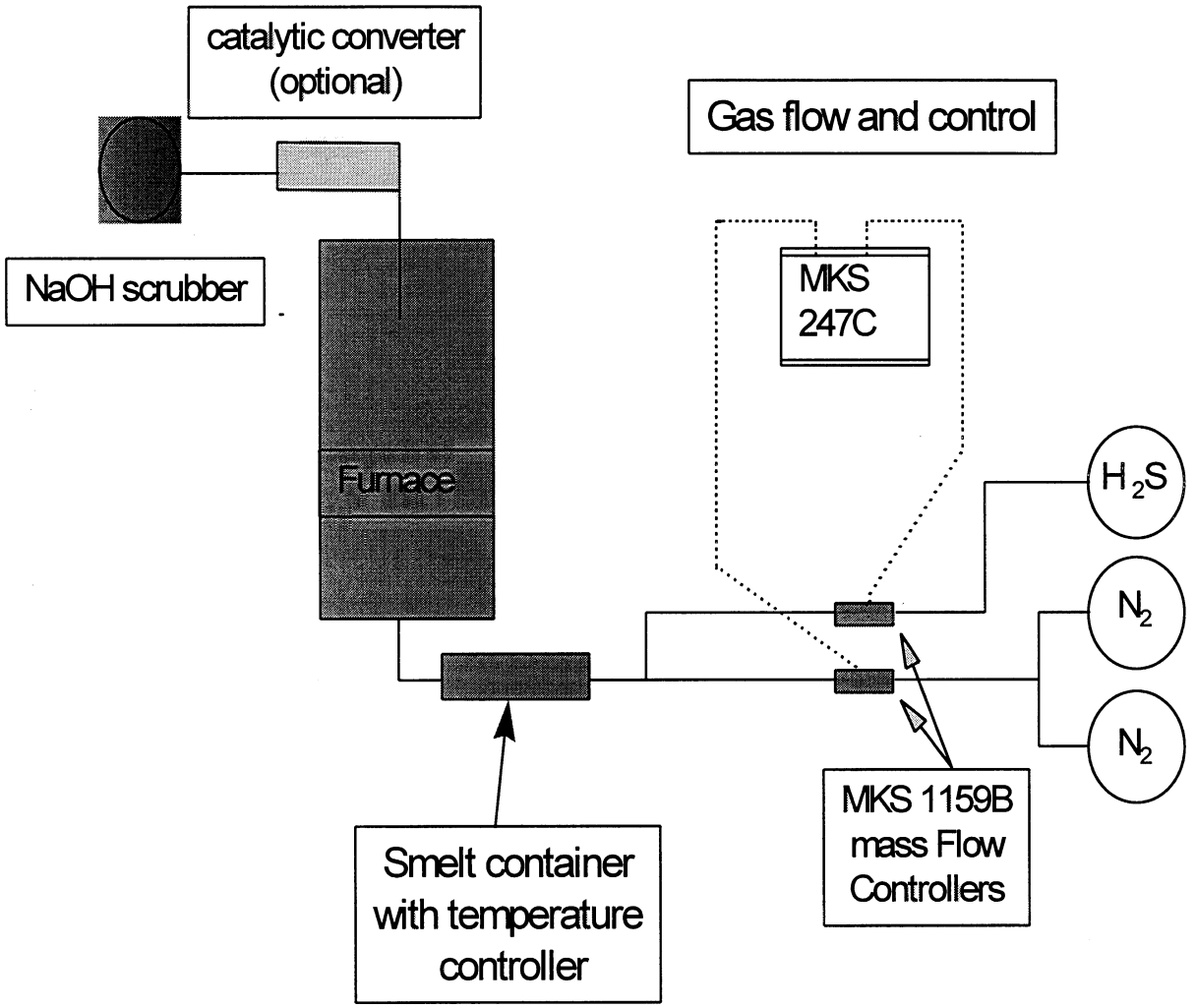

Figure 17. Experimental setup for the smelt tests.

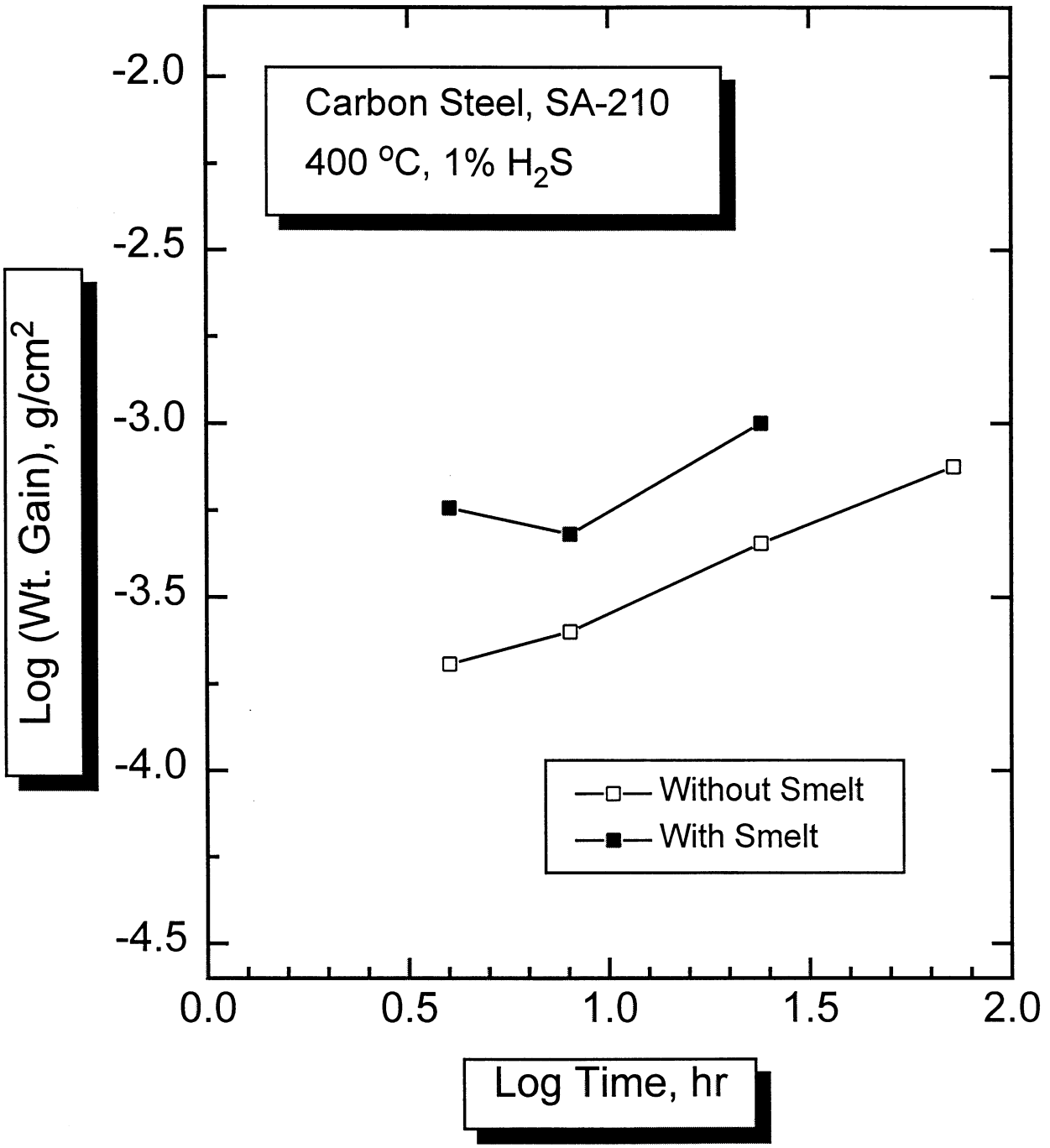

Figure 18. SA-210 carbon steel specimens tested in 1% H_2S at 400°C with or without the presence of smelt.

Task 2 Corrosivity Monitoring

The objective of this task is to develop/identify a device to measure corrosion conditions, which can be later applied to real-time feedback about corrosion during service. Placement of these devices will be critical to successfully measuring the worst conditions, but an array should cover the most likely locations.

Subtask 2.1 Survey of Candidate Techniques (PPRIC is Subtask Leader)

The objective of this subtask is to identify and prioritize candidate techniques to measure local environmental conditions or corrosion beneath frozen smelt as well as in the bulk environment. The measurements will ultimately be used to determine the corrosion conditions over some finite time period, so the technique must be capable of being integrated to obtain averages, which can be linked to the real boiler performance over some period of operation. These techniques may be based on electrochemical measurements, electrical resistance, or surface layer activation, as an example.

Current Status:

At the last TAG meeting, 3 candidate technologies were chosen from a list of 14 for further exploration. These technologies include:

a) Electrical Resistance Probes
b) Electrochemical Probes
c) Thin Layer Activation Probes

It was decided that more details should be sought on the most promising techniques for monitoring corrosivity, with a view of finding out what steps are necessary to install the appropriate instrumentation in an operating recovery boiler. Efforts have been directed towards collecting information on electrical resistance probes and thin layer activation/neutron activation. PPRIC is actively pursuing this task and has submitted a draft report on these technologies. The final report of this technology survey is expected to be ready by the end of March 1997.

Goals For FY 1996-97 (September 1997)

Task 1

Database design will be completed. Data from the papers identified so far will be entered into the database.

Most of the gaps identified, so far, in published data will be filled by generating experimental data at IPST.

Task 2

Subtask 2.1

Identification of corrosion monitoring technology will be completed.

Subtask 2.2 Laboratory Testing and Optimization

A device, or devices, will be constructed to test the concept and develop an understanding of the critical parameters that control performance. The device will need to be tested over the temperature range of whitewall tubes, the expected values of sulfur and oxygen partial pressures, and in the presence of solid salts, which comprise frozen smelt. Once these parameters are established, the device will be optimized to function in operating boilers. These tests will be carried out in laboratory furnaces using the same apparatus as used for the database generation task. Parameters such as stability of signal, reproducibility, and comparison to weight loss coupon results will be investigated.

Technical Program Review

Exploratory Project/Student Project

Project Title: Stress Corrosion Cracking of Composite Tubes in Kraft Recovery Boilers

Project Staff: P. Singh

OBJECTIVES :

To study environments in kraft recovery boilers that may cause stress corrosion cracking of 304-L stainless steels.

INTRODUCTION :

Composite tube cracking in kraft recovery boilers is one of the major safety concerns of recovery boilers. Results of the ORNL investigation and other published results indicate that the composite tube cracking in kraft recovery boilers may be due to SCC. It is not clear as to what environments are responsible for these failures.

At IPST, an exploratory project was started to investigate the possible stress corrosion cracking (SCC) mechanisms which can operate on the composite tubes. The following are the main objectives of this project:

1) To study the microstructural changes occurring in the composite tubes during operation and their effects on SCC susceptibility of 304-L stainless steel in recovery boiler environments.
2) To explore tendencies of various wash water compositions and different constituents of wash water to cause SCC of 304-L stainless steel.
3) To study other environments in the recovery boilers during the shut down condition which may cause stress corrosion cracking of 304-L stainless steel.

The initial set of tests using U-bend specimens is already being done. Slow strain rate tests will be carried out to screen and study the possible wash water constituents, which

are capable of causing stress corrosion cracking of stainless steel composite tubes. A systematic study will address some of the present cracking problems as well as indicate other possible mechanisms of stress corrosion, which can possibly operate in the recovery boiler environments. Part of this project is anA-190 (M.S. research) project for Daniel Andrews-Wilberforce.

CORROSION IN CLOSED CYCLE MILLS

PROJECT F019

ANNUAL RESEARCH REVIEW

March 26, 1997

Preet M. Singh

Gregory J. Fonder

Institute of paper Science and Technology
500, 10th Street, N.W.
Atlanta, GA 30318

TECHNICAL PROGRAM REVIEW

Project Title:	CORROSION IN CLOSED CYCLE MILLS
Project Number:	F019
Division:	Chemical and Biological Sciences
Project Staff:	P. Singh, G. Fonder
FY 96-97 Budget:	$140,000

Program Objectives:

To identify key corrosion and materials-related issues, which may impact the successful implementation of various closed mill scenarios and provide support to maximize the potential of these new technologies.

Summary of Results:

This project was started with the literature search to understand different mill closure procedures, which the pulp and paper industry has adopted or may adopt in the future. The literature search is not complete yet, but this status report includes a list of published literature that we have collected so far and also lists some of the corrosion-related concerns of these authors. The first draft of the literature review is expected to be finished by July 1997. It will be sent to the PAC members for their review and comments.

Design of mill closure, materials used, corrosion related problems, and general effects of water closure in the paper machine area and the bleach plant/pulp mill areas are different. Therefore, to handle this project more effectively, it has been divided into two major tasks:

1. **Task 1 Effects of white water closure on corrosion of the paper machine**
2. **Task 2 Effects of bleach plant closure on corrosion of the existing equipment**

It was decided to start with Task 1 of this project. Since the fall 1996 PAC Meeting in Chicago, we have made some progress in this direction. Work on this project started in January 1997 due to lack of the manpower for the ongoing projects in the corrosion area. Recently, an offer has been made for the position of senior technician in the corrosion and materials engineering group. This will give us the required resource to carryout this project at a desired pace.

Task 1 Effects of white water closure on corrosion of the paper machine

There are different designs of paper mill closure as well as different degrees of water reuse, which have been described in the literature.[1-16] Even though there are similarities in the overall philosophy of mill closure but, changes in the closure design may have significant effects on the resulting local environments and their corrosivity. Local environments, that equipment may get exposed to, may also vary from mill to mill. Because of these uncertainties in the published literature, we have adopted a parallel experimental approach to understand this problem from a materials point of view. Experiments are designed to study the effects of closure on the existing materials used in the pulp and paper industry. Laboratory experiments will be done on commonly used paper machine materials in simulated white water environments, representing different scenarios of paper mill closure. The main objective of the experimental project is to determine the limits of the environmental changes that can be safely handled by the existing materials used in the pulp and paper industry. After initial results, this project can be further extended to the new metallic and nonmetallic materials.

During the literature search, many relevant papers[1-56] in this area have been collected. A list of these papers and relevant publications in other languages is included at the end of this report.[57-71] This list is not complete by any means; however, these papers have helped us in understanding some of the major concerns so that laboratory experiments can be designed to address them. Papers collected so far can be divided into six major categories:

1) Design related with speculation on effects of closure on corrosion.[1-17,36, 39, 40, 42, 50-54, 56].

2) Mill survey results on corrosion in closed mills.[4, 14,16,20, 25, 73]
3) Field results on corrosion in closed mills. [17-30, 32, 34, 38, 41, 44, 46, 51, 52]
4) Laboratory studies in simulated environments. [18, 38, 46, 47]
5) Papers on material selection and other proposed corrosion mitigation schemes for closed paper mills.([31, 33, 35, 37, 42, 49, 51, 52, 55]
6) Microbial corrosion problems in closed mills.[26-30, 38, 41, 45, 48, 54, 64]

There are some exceptions, but the major areas of concern related to white water closure, listed by most of the papers collected so far, are summarized here.

1) Higher concentrations of chloride and sulfate ions in the closed white water systems.
2) Scaling problems due to increases in the concentrations of soluble and insoluble chemicals.
3) Increase in the temperature of white water.
4) Higher soluble organic compounds.
5) Higher microorganism activity (mostly anaerobic due to a decrease in oxygen solubility at higher temperatures) and its effects on corrosion, slimes and smell.

The general theme of papers, which reported survey results from paper mills with various degrees of closure, was that closure resulted in increased corrosion in these mills.[4, 14, 16, 20, 25]

A number of papers[16] discuss various white water closure designs and their effects on the environmental changes in this system. These papers do not talk about the corrosion issues in particular, but have predicted higher corrosion in closed white waters.

Some studies[31, 33, 35, 37, 42, 49, 51, 52, 55] have described material selection or some chemical control methods for the closed white water systems to mitigate corrosion. Generally, the use of biocides is recommended to fight microbial activities.[30, 41, 54] There is also some concern about increased concentrations of felt cleaning agents in the closed system and their adverse effects on corrosion in paper machines.[31] Roll manufacturers are

concerned about anticipated corrosion problems due to decreased pH, increased chloride, higher temperatures, and increased organic activities in the white water systems.[33]
An experimental study[46] conducted to simulate a particular design of white water closure has shown that the uniform corrosion rates of 304-L stainless steels were not significantly increased in recycled white water; however, the other forms of corrosion such as pitting corrosion and stress corrosion cracking susceptibilities of 304-L increased considerably.

At least one paper[64] has raised their concerns over the increase in sulfate levels in white waters above 3 g/l, which may deteriorate the reinforced concrete installations in effluent purification systems. They have recommended the use of polymer coating to prevent this effect.

Experiments in the simulated closed white water environments and further literature searches will help us understand the effects of water closure on existing materials.

PROJECT GOALS: (until end of FY 96-97)

1) To complete first draft of literature review by July 1997 and send it to PAC members for their review.
2) Start a set of experiments to test selected materials in the simulated close-white water environments to their performance limits.

GOALS FOR FY 97-98

1) Complete the final version of the review paper on effects of closure in white water systems.
2) Continue with experimental test program in closed white water systems.
3) Start literature review and test program on pulp mill/bleach plant closure.

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Corrosion of Composite Tube Air Ports in Kraft Recovery Boiler– Cr_2O_3 Solubility in NaOH

By Matthew Estes, Alan Rudie, and Jeffery Colwell

Abstract

Composite tubes in kraft recovery boiler air ports can experience severe corrosion. One possibility is the corrosion is caused by molten NaOH. The corrosion of stainless steel in molten salts is dependent upon maintaining the protective Cr_2O_3 film formed on the surface. The goal of this project was to measure the solubility of Cr_2O_3 as a function of the basicity of NaOH. Plots of the chromium ion concentration indicate a minimum solubility at -log $a_{(Na_2O)}$ of 8.2. The data support two mechanisms for dissolution of the Cr_2O_3. The basic dissolution had a slope of -0.988, consistent with the formation of Na_2CrO_4. The acidic dissolution had a slope of 1.48, consistent with the formation of Cr^{3+}. The results from weight loss experiments on chromium metal were then compared to the solubility curves for Cr_2O_3 to confirm that metal oxide solubility was the rate limiting step in the corrosion mechanism. The weight loss experiments on chromium metal also confirmed that the corrosion rate was a function of the basicity of molten NaOH. Understanding the mechanisms and the environment in which minimum solubility occurs for chromium oxide allows a solution to be proposed to lessen the composite tube air port corrosion of kraft recovery boilers.

Introduction

In recent years, the frequency of corrosion in recovery boiler air ports has risen dramatically throughout the pulp and paper industry (1-5). The increase coincides with the growing use of composite tubes, which are fabricated with a stainless steel outer shell and carbon steel inner body. A unique characteristic of air port corrosion is that the stainless steel is rapidly attacked, exposing the carbon steel underneath. Stainless steel corrosion rates up to 150 mils per year (mpy) have been measured (1-5). After completely consuming the stainless steel, corrosion of the underlying carbon steel occurs at a rate of 10 mpy (1-5). However, there is some concern that the carbon steel can suffer sulfidation corrosion, which was the reason for using composite tubes in air ports.

Molten sodium hydroxide has been postulated as a possible cause for corrosion at air ports (1-3, 5). The severity and uniformity of corrosion are consistent with a molten salt reaction. It has been suggested that sodium hydroxide vaporizing from the smelt bed can migrate to the air port (1). The walls of the air port at 275 to 500°C are relatively cool (4-6). At these temperatures, sodium hydroxide vapors would condense on the waterwall tube surface as a liquid.

There is some evidence for NaOH being present at kraft recovery boiler air ports. Colwell and Fonder collected deposit samples on a cooled probe and measured the melting point *in situ* inside a kraft recovery boiler. Analysis of a limited deposit showed a Na:K ratio of approximately 6:1. The melting points measured yielded a value close to the theoretical melting point of NaOH:KOH of 6 to 1 ratio (3).

Laboratory experimentation has shown that molten sodium hydroxide corrodes stainless steel faster than carbon steel (3). Other corrosive mechanisms in addition to molten NaOH may take place as suggested by Falat (6), but they do not explain why stainless steel corrodes faster than carbon steel.

Theory of molten salt reactions

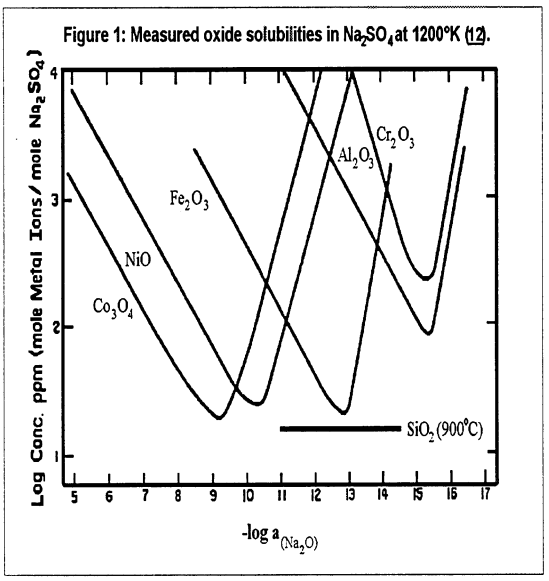
The stability of an oxide layer on a metal is a function of the oxide's thermodynamics, growth kinetics, and the dissolution of that oxide in the environment. Solubility of an oxide can be defined as the maximum weight of metal ions in solution divided by the weight of the solution. Solubility of a nominally protective oxide is often a function of the salt basicity; where solubility is the defining mechanism, the corrosion rate should also be a function of basicity.

Basicity of a molten salt is defined on the basis of the dissociation of the compound, in this case, NaOH:

$$2\,NaOH = Na_2O + H_2O \qquad (1)$$

For sodium hydroxide, sodium oxide is defined as the Brönsted base because it accepts a proton, and water is defined as the Brönsted acid because it donates a proton. Basicity, for NaOH, can also be defined by $-\log a_{(Na_2O)}$, analogous to the definition of pH.

A considerable volume of work has been reported in the literature showing the solubility of different metal ions plotted as function of basicity as shown in Figure 1 (7-15).



The plots have basicity values along the x-axis and the solubility limit of the metal oxide along the y-axis. These plots show the basicity conditions that give the minimum solubility for a particular metal oxide. If the basicity conditions for a metal oxide is located to the left side of the minimum, the material undergoes a basic dissolution mechanism such as:

$$M_xO_Y + O^{2-} = M_xO^{2-}_{Y+1} \qquad (2)$$

where M = metal O = oxygen

If the basicity conditions for a metal oxide is located to the right side of the minimum, the material undergoes an acidic dissolution mechanism, which is:

$$M_xO_Y = X\,M^{a+} + Y\,O^{2-} \qquad (3)$$

Thus, the location on the curve provides information about which type of dissolution is occurring.

In addition, based on various assumed soluble ions, the dependence of the solubility of a particular ion on basicity can be related to the experimental slope of the curve. An example of acidic dissolution would be:

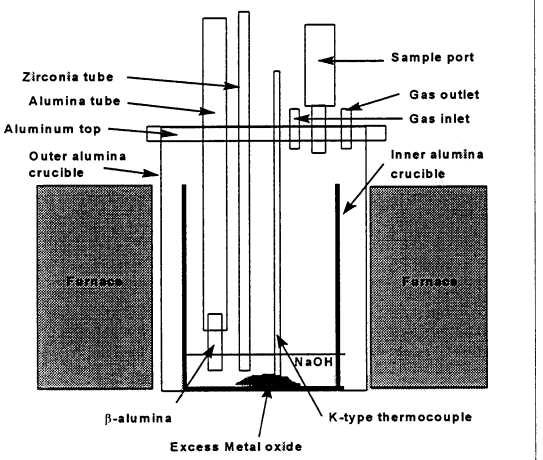
$$\left(\frac{-\log M^{a+}}{-\log O^{2-}}\right) = \frac{Y}{X} \qquad (4)$$

Agreement between the experimental slopes and theoretical slopes based on stoichiometric equations can be used to confirm the identity of the soluble ion (2).

Equipment

A schematic cross section of the furnace, the crucibles holding the sample, and the electrodes to measure basicity is shown in Figure 2.

Figure 2: Equipment setup



The ceramic crucibles were surrounded by a cylindrical radiant furnace that provided uniform heating. Temperature was measured with a calibrated K-type thermocouple protected by an α-alumina tube and was controlled by a CN3201 Omega® controller. An aluminum top and a silicone O-ring encapsulating in Teflon®, sealed the top of the crucible. Port holes fitted with Cajon® vacuum fittings with Viton® O-rings provided access to the reactor for the thermocouples, gas inlet and outlets, and electrodes.

Electrodes were inserted into the melt to measure the basicity (16-17). The electrode system consisted of a combination of a β-alumina probe and a zirconia probes. β-alumina ($Al_2O_3 * 5\ Na_2O$) conducts sodium ions exclusively. The ß-alumina tubes were purchased from Polyceram and attached using a Durabond 989™ adhesive to an α-alumina tube to minimize the expense. The inside of the tube was filled with sodium metal, in contact with a platinum wire that was routed outside and sealed. A potential across the ceramic tube wall results from a difference in sodium activity.

Zirconia fully stabilized with yttria ($ZrO_2 * Y_2O_3$) conducts oxygen ions exclusively. The inside end of a closed-end tube was painted with three coats of platinum paste and attached to a platinum wire. The tube was open to the air and thus uses the oxygen in air as a reference. A potential across the ceramic tube wall results from a difference in the oxygen activity.

The half-cell reaction at each electrode is as follows:

Oxidation: 2 [$Na \rightarrow Na^{+} + e^{-}$] (5)

Reduction: ½ $O_2 + 2e^{-} \rightarrow O^{2-}$ (6)

Using the Nerst equation, it follows that

$$E = E° - \frac{RT}{ZF} \ln a_{(i)} \quad (7)$$

where Z represents the moles of electrons participating in the reaction. For our case with NaOH, equation (7) becomes

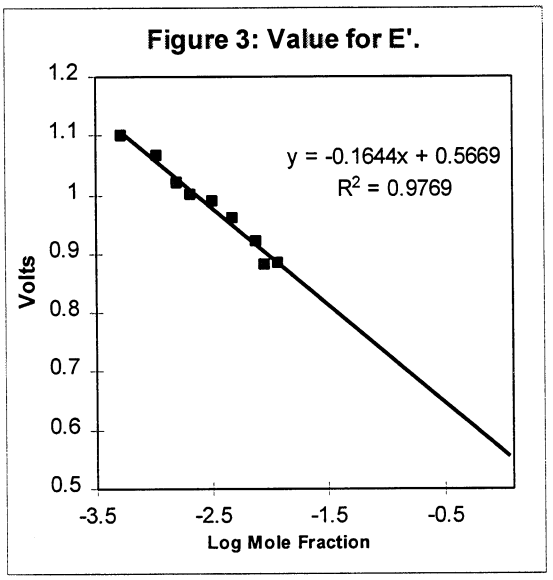
$$E = E° - \frac{RT}{2F} \ln a + \frac{RT}{F} \ln (Na) + \frac{RT}{4F} \ln P(O_2) \quad (8)$$

Using pure Na metal as the reference, in the standard state (Na) is unity and ln (Na)=0.

$$E = E° - \frac{RT}{2F} \ln a_{(Na_2O)} + \frac{RT}{4F} \ln P(O_2) \quad (9)$$

R is equal to 8.314 J * mol^{-1} * K^{-1}, and F is equal to 96484.6 C/mol. The temperature, T, was held constant at 773 K for the experiments. Because atmospheric air was the reference for the zirconia tube, the $P(O_2)$ was equal to 0.21 atm. By measuring the voltage, E, the resultant activity of sodium oxide was used to determine the basicity of the sodium hydroxide melt.

The E° value in equation (9) was experimentally determined as follows: first, the sodium hydroxide was completely dried at 500°C under nitrogen gas for three days to remove excess water and contaminants. Then, the basicity was changed by adding sodium oxide to the sodium hydroxide in different concentrations, and the corresponding voltage was measured. A plot of the mole fraction of sodium oxide versus the measured voltage is shown in Figure 3.



Extrapolating the line to zero sodium oxide content gives E° = 0.567.

For the experiments, sodium oxide was added to make the NaOH more basic. Sodium oxide pellets were purchased from Aldrich®.

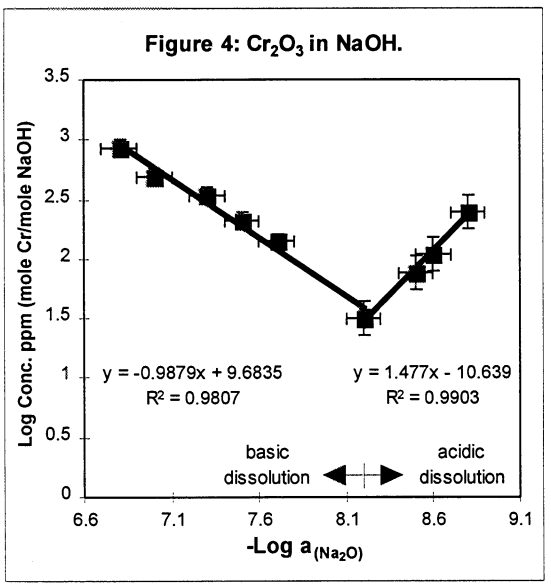
To make NaOH more acidic water vapor was added by bubbling the carrier gas through a water column fitted with a polyurethane frit. By fixing the water column temperature and assuming saturation, which was tested by Schwerdtfeger, the vapor pressure was determined (18).

Samples for chemical analysis were collected by inserting a ceramic rod through a ball valve on the aluminum top. The depth of rod insertion was calibrated so that samples of approximately the same size and nearly the same area were obtained. The cold rod caused the sample to freeze to the rod as it was withdrawn from the melt. The sample was then quickly scraped off with ceramic tweezers into a volumetric flask partially filled with deionized water. The weight change of the flask was recorded. The flask was then filled to the mark with deionized water and stored until analyzed. Four replicate salt samples were taken at each basicity.

Chromium concentration was measured using a Perkin Elmer Optima 3000 Dual View Inductively Coupled Plasma (ICP) Spectrometer. Standards were prepared, values loaded into the computer, and then compared with unknown samples using EPA's guidelines for solid waste (19). The optimal conditions for the ICP had been found to be a pressure of 70 psi for argon and wavelength 267 nm for chromium. Chromium gave a linear response from 0.04 ppm to 100 ppm. Each unknown sample was analyzed three times, and the average value was reported.

Results and Discussion

Results for the chromium concentration vs. basicity are summarized in Figure 4 below.



Each basicity condition shown in Figure 4 is a mean of three values. Equilibrium was ensured at a given basicity by measuring until the concentration did not change over three days. Chromium oxide was found to have a minimum solubility at a basicity of 8.2. The solid line represents the least squares best fit of the data. Basicity error bars were estimated at -log $a_{(Na_2O)}$ ± 0.1 based upon fluctuations in the voltage readings. Concentration of chromium error bars show ± one standard deviation.

If the dissolution reaction for basic conditions is assumed to be:

$$Cr_2O_3 + 2\,O^{2-} + \frac{3}{2}\,O_2 = 2\,CrO_4^{2-} \qquad (10)$$

At constant $P(O_2)$,

the theoretical slope for the reaction is given by:

$$\left(\frac{-\log CrO_4^{2-}}{-\log O^{2-}}\right) = -1 \qquad (11)$$

The measured value of -0.9879 is in very good agreement with theory. Also, the melt was yellow in color, which is consistent with the formation of chromate (20).

If the dissolution reaction for acidic conditions is assumed to be:

$$Cr_2O_3 = 2\ Cr^{3+} + 3\ O^{2-} \qquad (12)$$

The theoretical slope for the reaction is given by:

$$\left(\frac{-\log Cr^{3+}}{-\log O^{2-}}\right) = \frac{3}{2} \qquad (13)$$

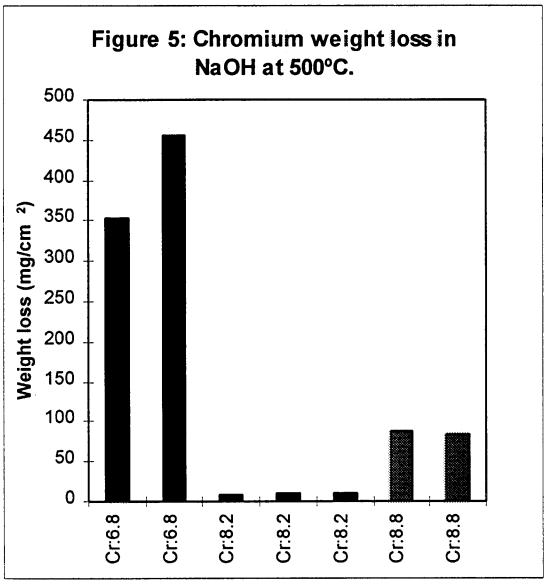
The measured value of 1.477 is in very good agreement with theory. Also, the melt was green in color, which is consistent with the formation of chromium ions (20).

To further confirm that the mechanism for dissolution had changed, the oxidation state of the chromium ion was determined. A chemical method described by Cranston and Murray was used (21). Chromium (III) was scavenged by reacting the solution with 0.01 M iron(III) hydroxide at pH 8. The chromium was precipitated and collected on a 0.45 μm Nucleapore™ filter precleaned with 12 M HCl. The chromium complex was then dissolved in 6 M HCl and analyzed by ICP. Chromium (VI) and chromium(III) are both precipitated by reacting the solution with iron(II) hydroxide at pH 8. The iron(II) was oxidized to iron(III), and the chromium(VI) was reduced. The precipitated chromium was dissolved in 6 M HCl and analyzed as before. Chromium (VI) was determined by the difference.

Results indicate that the mechanism for dissolution had changed under different basicity conditions on either side of the minimum. Cr(III) was the dominant species at -log $a_{(Na_2O)}$ of 8.8, and Cr(VI) was the dominant species at -log $a_{(Na_2O)}$ of 6.8. The change in the oxidation state of chromium confirms that the mechanism changed from basic to acidic dissolution.

Weight loss experiments

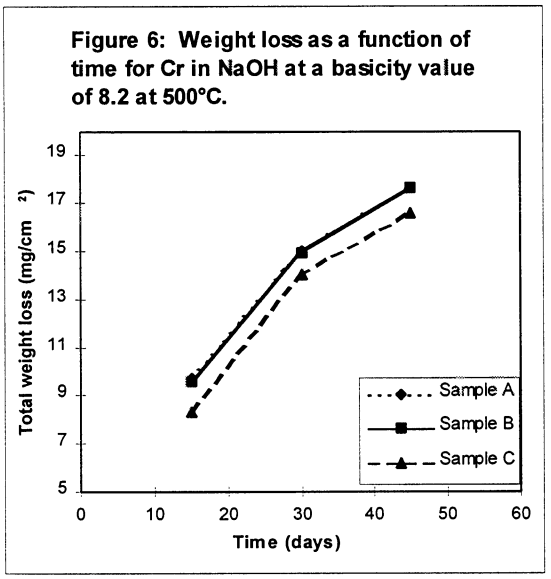
Weight loss experiments were performed using chromium metal in molten NaOH at basicity values of 6.8, 8.2, and 8.8. The three basicities selected represented basic dissolution, the solubility minimum, and an acidic dissolution, respectively. Figure 5 shows the results of the weight loss measurements performed at different basicities.



The weight loss variation can be predicted from the basicity and solubility curves. The chromium oxide solubility results in Figure 4 show that the solubility was at a minimum at a basicity value of 8.2. The weight loss of chromium metal is also low at a basicity value of 8.2.

At basicities of 6.8 and 8.8, the solubilities were much higher, which should lead to higher weight loss. Furthermore, the weight loss at a basicity value of 6.8 should be higher than at 8.8 based upon the solubility curve in Figure 4. Weight loss experiments with chromium metal at basicities of 6.8 and 8.8 in Figure 5 showed the predicted increase in weight loss. Therefore, basicity, which determines the solubility, does affect the weight loss of chromium metal.

In addition, three samples of chromium metal were placed in NaOH at a basicity value of 8.2. The minimum of the chromium oxide solubility was chosen to determine the effect of time on weight loss. After 15 days, the samples were removed and cleaned with water to remove excess NaOH. The samples were then ultrasonically cleaned for 5 minutes in acetone and dried in a desiccator prior to weighing. The same samples were replaced in the furnace with fresh NaOH for an additional 15 days. In figure 6, the results were graphed showing the weight changes of three 15-day trials.



Samples taken from the melt were analyzed by the ICP. The samples were yellow, indicating the presence of chromate, so the basicity was slightly on the basic side of the minimum. The average results are summarized in Table 1.

Table 1: Analysis for chromium by ICP

	Log chromium (ppm)
1st 15 days	2.70
2nd 15 days	1.18
3rd 15 days	0

The results show that the weight loss decreased each time a new trial began. The chromium ions in the melt also identically decreased in each trial until no chromium was detectable.

The kinetic reaction is a first-order reaction. Visually, a dark green, fairly compact scale formed on the test pieces that was strongly adherent to the metal. Because the chromium oxide was minimally soluble in NaOH under the tested conditions, the chromium oxide was able to form a passive layer, which reduced the rate of corrosion. Because the melt was replaced at each 15-day interval, the drop in corrosion rate was not due to the melt becoming saturated.

Conclusion

The solubility of Cr_2O_3 was determined as a function of basicity. The results clearly show a minimum solubility at -log $a_{(Na_2O)}$ of 8.2. The data suggest two mechanisms of dissolution of chromium oxide in molten NaOH. Basic dissolution (basicity values < 8.2) formed chromate, and acidic dissolution (basicity values > 8.2) formed chromium ions. Analysis of the oxidation state of chromium confirmed the products.

The solubility curves successfully predicted the variation in the weight loss of chromium metal. Chromium coupons at -log $a_{(Na_2O)}$ of 8.2, which is the minimum solubility of chromium oxide in NaOH, developed a green film that successfully lessened the corrosion.

Controlling conditions in the kraft recovery boiler air ports that establish a minimum solubility condition should lead to a lower corrosion rate of composite tubes. The basicity of a NaOH deposit in a kraft recovery boiler could be controlled by the amount of water vapor in the incoming air to reduce the corrosion rate and provide significant cost savings. The practicality of such an approach would have to be demonstrated. Addition factors, such as the presence of and effect of other metal oxides and chemical species should be investigated further.

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